COMPARISON OF THE EFFICIENCY OF A THERMO-CHEMICAL PROCESS TO THAT OF A FUEL CELL PROCESS WHEN BOTH INVOLVE THE SAME CHEMICAL REACTION

A Thesis

by

SESHU PERIAH BULUSU

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2007

Major Subject: Mechanical Engineering

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Approved by:

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Committee Members,	Thomas Lalk
	Sharath Girimaji
Head of Department,	Dennis O'Neal

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ABSTRACT

Comparison of the Efficiency of a Thermo Chemical Process to that of a

Fuel Cell Process When Both Involve the same Chemical Reaction. (August 2007)

Seshu Periah Bulusu, B.Tech. Mechanical Engineering, JNTU, India

Chair of Advisory Committee: Dr. Kalyan Annamalai

This work assesses if a plausible theoretical thermo-chemical scheme can be conceived of, that is capable of extracting work from chemical reactants which can be compared with work produced by a fuel cell, when both processes are supplied with the same reactants. A theoretical process is developed to convert heat liberated from a chemical reaction to work. The hypothetical process is carried over a series of isothermal chemical reactor - heat engine combinations. Conducting the chemical reaction and work extraction over a series of temperature steps minimizes irreversibilities that result from the chemical reaction and heat transfer.

Results obtained from the numerical calculations on the scheme confirm that when a large number of reactors-engine combinations are used, irreversibility of the proposed hypothetical reactor-engine combination can be reduced to zero. It is concluded from the results, that the theoretical model is as efficient as a fuel cell when both have the same chemical reaction under identical conditions. The effect of inert gas chemistry on the process has also been observed. It is determined from the results that the chemistry of the inert gas does not affect the proposed process. It is determined from results of a parametric study on the composition of inert gas, that the reduction of inert gas does not significantly improve the efficiency of the proposed process.

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TABLE OF CONTENTS

LIST OF FIGURES

FIGURE Page

LIST OF TABLES

NOMENCLATURE

$C_{p,k}$	Specific heat coefficient of species k
E	Energy of the system
G	Gibbs energy
g_k	Specific Gibbs energy of species k
H	Enthalpy
h_k	Specific enthalpy of species k
$K°(T)$	Equilibrium constant at temperature T
m_i	Mass of species i
N_k	Number of moles of species k
P	System pressure
p_k	Partial pressure of species k
P°	Atmospheric pressure
Q	Heat transfer across the system boundary
$\overline{R}$	Universal gas constant
S	Entropy
s_k	Specific entropy of species k
T_{ad}	Adiabatic flame temperature
T_b	Temperature of boundary for heat transfer
$T_{C,L}$	Temperature of combustion (Lutz)
$T_{C,H}$	Temperature of combustion (Hassanzadeh)
$T_{C,B}$	Equivalent Carnot temperature
T_o	Ambient temperature (298°K)
T_L	Lower temperature TER
T_H	Higher temperature TER
W	Work transfer across the system boundary
W_{opt}	Optimum work
X_k	Mole fraction of species k
ΔG_R	Gibbs energy change for reaction
ΔH_R	Enthalpy change for reaction
ΔS_R	Entropy change for reaction

ΔS_W	Entropy change of working fluid

Greek Symbols

η_{avail}	Availability efficiency
η_{th}	Thermal efficiency
σ	Entropy generation
σ_{ad}	Entropy generation due to adiabatic combustion
ψ_k	Availability of species k

Superscript

0	Resitricted dead state condition

Subscripts

0	Atmospheric conditions
k	Species index
cv	Control volume
P-R	Difference of value from products to reactants

INTRODUCTION

Almost all processes require energy either in the form of electrical or mechanical work. Fossil fuel and other naturally occurring chemicals contain chemical energy which can be converted to work. Conventional heat engines employ combustion of a chemical (fuel) to obtain thermal energy which is converted to mechanical energy and then to electricity. A fuel cell uses electron transport in converting chemical energy directly to electricity.

Attempts have recently been made to compare the efficiencies of heat engines and fuel cells. A fuel cell in general observed to have higher efficiency when compared to a heat engine. Heat engines suffer from losses when converting chemical energy to thermal energy. Additional losses are incurred in converting thermal energy to work. The efficiency of a heat engine is calculated based on a cyclic process. On the other hand a fuel cell involves a single chemical reaction process. This was one of the reasons considered why the efficiencies of a fuel cell and a heat engine cannot be compared.

Fuel cells are believed to be highly efficient compared to conventional heat engines. Heat engines require thermal energy as input for conversion to mechanical energy. This requires that chemical energy be converted to thermal energy using a chemical reaction (combustion). In principle, all chemical reactions are irreversible and this leads to the concept of lost work (from availability analysis) within the combustor. In addition conversion of heat into work is limited by the second law (even for reversible heat engines) and this reduces the overall efficiency of the system. Fuel cells on the other hand directly convert chemical energy to high quality electric work without having to go through the thermal phase. This significantly improves the overall efficiency of the system. Fig. 1 describes the schematic of working principles involved in both processes.

This thesis follows the style of International Journal of Hydrogen Energy.

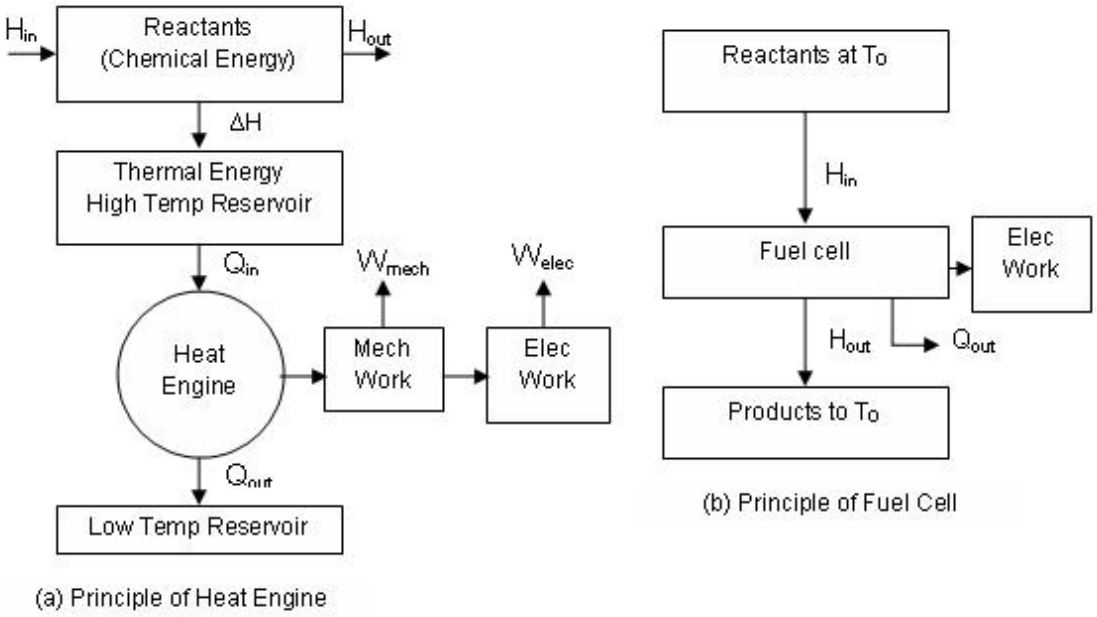

Fig. 1. Illustration of difference in working principles of heat engines and fuel cells.

As with the case of any two power generating units, there has always been a comparison between the efficiencies of heat engines and fuel cells. Because of the fewer losses and direct conversion to high quality work, fuel cells always seemed to be more efficient. The popular opinion is that fuel cells are not in a cyclic process and hence are not constrained by the Carnot efficiency. This has lead some people in the past to believe that a fuel cell is not constrained by the second law.

While the above statements summarize the popular opinion on principle of energy conversion of fuel cells, Lutz et al., [1] contended that theoretically, a fuel cell and an ideal heat engine with same fuel input must have the same efficiency. The objective of their work is to "…dispel the misconception that an ideal fuel cell is potentially more efficient than an ideal heat engine". They proposed a model of chemical reactor and heat engine combination to extract work from Hydrogen (H_2). In the reactor, there is combustion of H_2 given by the equation $H_2+½O_2 \rightarrow H_2O$. Heat liberated from the combustion reaction is supplied to a Carnot engine to produce work. A fuel cell uses the

same chemical reaction given above to convert chemical energy to electric work. As Lutz's model and a fuel cell have the same set of reactants and products, both their efficiencies can be compared.

Lutz defined $T_{C,L}$ as the maximum temperature the chemical reactor can attain. Mathematically $T_{C,L}$ is attained when the change in Gibbs free energy ($\Delta G°$) of the reaction is zero. Here, $\Delta G°_R = \Delta°H_R - T*\Delta°S_R$. For the combustion reaction given above $T_{C,L}$ is calculated as 3802°K. Lutz's computed the Carnot efficiency of their model based on $T_{C,L}$ and compared it with the efficiency of a fuel cell and concluded that the efficiency of their ideal model and that of a fuel cell were comparable.

Their combustion model was based on three main assumptions. The first one is complete combustion of H_2 at high temperatures ($T_{C,L}$). The other assumption is the temperature of reactor maintained at $T_{C,L}$ during the combustion process. Constant enthalpy of reaction (combustion reaction mentioned above) (ΔH_R) and entropy of reaction (ΔS_R) for a range of temperatures till 5000°K were also assumed.

Hassanzadeh and Mansouri [2] argued that the assumptions made by the Lutz model are incorrect as combustion of H_2 reaches equilibrium compositions at high temperatures. Hassanzadeh redefined the temperature at which the reactor can be maintained ($T_{C,H}$). $T_{C,H}$ gives a much lower Carnot efficiency for the Lutz model. Hassanzadeh used this result to conclude that "…..does not mean that the two systems should have the same maximum thermal efficiency when being fed the same amount of chemical reactants".

In view of the earlier statements in comparing the efficiency of fuel cells and heat engines, it is of interest to determine if an ideal heat engine can reach the efficiency of a fuel cell for the same chemical reactants. This involves determining the process for chemical combustion followed by work extraction. A model is to be developed for

reversible heat and work interactions to minimize irreversibility. Efficiency of the model is then compared against that of a fuel cell with the same chemical reaction

For the above comparison, consider an Energy Conversion System (ECS) depicted in Fig. 2. The ECS represents a generic process for conversion of chemical energy to work having heat interaction with the atmosphere. Since fuel cells and heat engines are both thermodynamics processes, the generalized scheme can represent either of them. Availability analysis is performed on the whole system to calculate the work done in both ideal cases. Efficiency of an ideal heat engine can then be compared to that of a fuel cell when the same chemical reactants are supplied in each case.

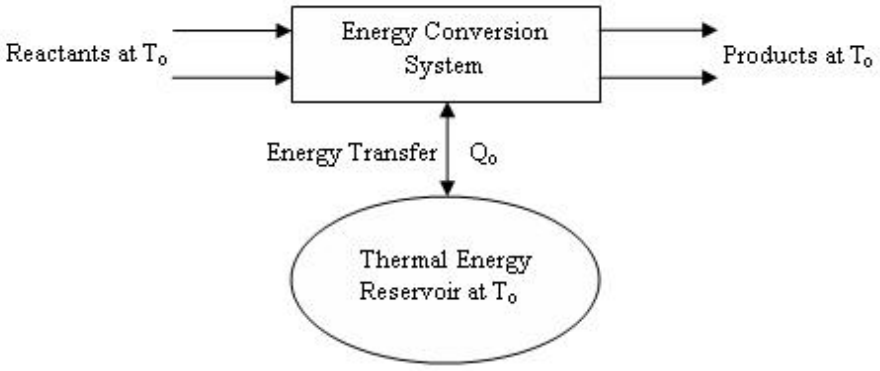

Fig. 2: Energy Conversion System (ECS) representing generalized schematic for conversion of chemical energy to work.

LITERATURE REVIEW

This section explains in brief, the working principle of fuel cells. It covers the fundamentals of thermodynamic principles considered for computation of efficiencies of energy conversion. It also covers the thermodynamic modeling of a fuel cell considered as a fundamental heat work interaction model. In addition, this section covers the concept of availability balance and its rate equation derived from basic first and second law equations.

Earlier work from Lutz et al. [1] (which compares energy conversion in fuel cells and ideal heat engines) is explained in detail. Hassanzadeh and Mansouri's paper which contradicts Lutz's work is also described in detail. The scheme of extraction of optimum work from products of adiabatic combustion is also discussed. Irreversibility due to a chemical reaction and due to mixing is discussed. A brief overview is given regarding the concept of chemical equilibrium.

Fuel Cell Operation

A Fuel cell is an electrochemical device for converting chemical energy to electrical energy using a chemical reaction [3]. It uses electron transfer across an external closed circuit to produce electricity. Though more than one electrolyte can be used in a fuel cell, the most popular and commercial version is the Proton Exchange Member (PEM) fuel cell. It is named after a non-conductive, proton permeable material which separates the anode from the cathode.

The primary reactants used in the PEM fuel cell are Hydrogen (fuel) and Oxygen (oxidizer). H_2 is supplied at the anode side and O_2 is supplied at the cathode side. A layer of Platinum is applied as catalyst to the electrodes (both side of the PEM). An external conductor closes the electric circuit from the anode to the cathode. At the anode, the

catalyst helps H_2 split into H^+ ions and electrons (e^-). This creates a potential difference between the electrically positive anode and the neutral cathode. As the PEM is non-conducting, the electrons migrate to the cathode using the only other route (the external circuit). The H^+ atoms (protons) diffuse through the PEM to the cathode. Protons electrons and the O_2 present at the cathode react to form water, which leaves the fuel cell as a product restoring the fuel cell to its original state. Maintenance of a potential difference between the electrodes is a continuous source for electricity.

The reactions in fuel cell can be summarized as follows:

At Anode: $H_2 \rightarrow 2H^+ + 2\ e^-$

At Cathode: $\frac{1}{2}\ O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O$

Net overall Reaction: $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$

O_2 supplied to the cathode can be pure or can be obtained from air. If obtained from air, for every kmole of O_2 required for the reaction, we need to supply 4.76 kmole of air (1 kmole of O_2 and 3.76 kmole of N_2). N_2 obtained with O_2 serves as an inert gas and does not contribute to the chemical reaction. Thus the overall reaction for the fuel cell does not change with the introduction of inert gas.

The typical operating temperature for PEM fuel cells is around 348°K. Fuel cell generators can incur installed costs of $10,000 /kW for continuous operation and $500 /kW for peaking loads.

Thermodynamic Background

Efficiency of Heat Engines and Fuel Cells

The thermodynamic efficiency of any heat engine going through a cyclic process is defined by the equation

$$\eta_{th} = \frac{W_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} \tag{1}$$

Q_{in} here represents the heat supplied to the system. In the ECS considered in Fig. 2, which can be applied both to fuel cell and a heat engine system, Q_{in} is the same as ΔH_R (Enthalpy of the reaction).

Carnot cycle sets the limit of efficiency that can be obtained for a heat engine operated between two thermal energy reservoirs. T_L represents the temperature of low temperature reservoir (sink) and T_H represents the temperature of the high temperature reservoir (source). The efficiency of the cycle for the pair of temperatures is given by

$$\eta = 1 - \frac{T_L}{T_H} \tag{2}$$

when T_L=T_0 (ambient temperature) and T_H = T (temperature at which higher temperature reservoir is maintained), Eq. (2) becomes

$$\eta = 1 - \frac{T_O}{T} \tag{3}$$

Consider a fuel cell operating on a flow process. From first law equation for an open system,

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{inlet} \dot{N}_k \bar{h}_K - \sum_{exit} \dot{N}_k \bar{h}_K \tag{4}$$

Entropy balance for the fuel cell process obtained from second law balance gives the following equation

$$\frac{dS}{dt} = \frac{\dot{Q}}{T_b} + \sum_{inlet} \dot{N}_k \bar{s}_k - \sum_{exit} \dot{N}_k \bar{s}_k + \dot{\sigma} \tag{5}$$

For the fuel cell process under steady state conditions, Eq. (4) reduces to

$$\dot{W}_{elec} = \dot{Q} + \sum_{inlet} \dot{N}_k \bar{h}_K - \sum_{exit} \dot{N}_k \bar{h}_K \tag{6}$$

and Eq. (5) reduces to

$$\frac{\dot{Q}}{T_b} + \sum_{inlet} \dot{N}_k \bar{s}_k - \sum_{exit} \dot{N}_k \bar{s}_k + \dot{\sigma} = 0 \tag{7}$$

Eliminating $\dot{Q}$ from Eq. (6) and Eq. (7) yields the equation

$$\dot{W}_{elec} = \sum_{inlet} \dot{N}_k \bar{g}(T, p_k) - \sum_{inlet} \dot{N}_k \bar{g}(T, p_k) - \dot{\sigma} T_b \tag{8}$$

$\dot{W}_{elec}$ represents the electric work delivered by the fuel cell.

$\bar{g}(T, p_k)$ is the Gibbs property for a species given by

$$\bar{g}(T, p_k) = \bar{h}_k - T\bar{s}_k(T, p_k) \tag{9}$$

where T is the system temperature and p_k is the species pressure in the composition.

Consider a fuel cell which has an input of 1 kmole of H_2, 0.5 kmole of O_2 and producing 1 kmole of H_2O. For ideal reversible conditions ($\dot{\sigma} = 0$), Eq. (8) gives the work output from a fuel cell and is equal to [4]

$$\bar{W}_{elec} = \frac{\dot{W}_{elec}}{\dot{N}_{H2}} = -\Delta G_R \tag{10}$$

Gibbs energy of reaction for fuel cell (H_2+½O_2→H_2O) is computed as

$$\Delta G_R = \bar{g}_{H2O}(T, p_{H2O}) - 0.5 * \bar{g}_{O2}(T, p_{O2}) - \bar{g}_{H2}(T, p_{H2}) \tag{11}$$

From Figure 1(b), it is seen that energy supplied to the fuel cell is H_{in}-H_{out} = ΔH_R where

$$-\Delta H_R = 0.5 * \bar{h}_{O2}(T, p_{O2}) + \bar{h}_{H2}(T, p_{H2}) - \bar{h}_{H2O}(T, p_{H2O}) \tag{12}$$

Using Eq (10) and Eq (12), efficiency of the fuel cell is given by

$$\eta_{th} = \frac{Sought}{Bought} = \frac{-\Delta G_R}{-\Delta H_R} = 1 - T\frac{\Delta S_R}{\Delta H_R} \tag{13}$$

Enthalpy of reaction for a forward reaction is negative and usually entropy change for the reaction is positive. But in certain cases, where the entropy change for reaction is negative, Eq. (13) yields an efficiency of more than 100%.

As explained by Lutz, the decrease in entropy for a fuel cell would imply absorption of heat from the atmosphere and conversion of additional heat to electrical work. Typically, the heat from ambient is 'free' and as such it is not included in definition of efficiency. However, for such cases, in order to have efficiency values less than unity, Lutz et al. [1] propose a generalized form for Eq. (13) as follows

$$\eta = 1 - T\frac{\Delta S_R}{\Delta H_R} \qquad (if\ \Delta S_R \geq 0)$$
$$\eta = 1 \qquad (if\ \Delta S_R < 0) \tag{14}$$

Writing Eq. (7) on mole basis and substituting $\bar{W}_{elec} = -\Delta G_R$ from Eq. (10), one can find the heat added or removed from an isothermal fuel cell (for every kmole of H_2 combusted) as

$$Q = T\Delta S_R$$

Availability Analysis

Availability equations are derived from the first and second law equations of thermodynamics. The first law equation for an open system is given by

$$\frac{dE_{c.v}}{dt} = \dot{Q}_{c.v} - \dot{W}_{c.v} + \sum_{inlet} \dot{m}_e e_t - \sum_{exit} \dot{m}_e e_t \tag{15}$$

Here e_t represents the total energy (enthalpy, kinetic and potential energies) of the species at that state point. $\dot{Q}_{c.v}$ represents $\dot{Q}_o + \dot{Q}_{R,1} + \dot{Q}_{R,2}$..... where $\dot{Q}_o$ is the total heat leaving the control volume to the ambience and $\dot{Q}_{R,1}$, $\dot{Q}_{R,2}$ represent thermal energy transferred to the control volume at temperatures T_1, T_2 respectively.

The second law balance for an open system is given by the equation

$$\frac{dS_{c.v}}{dt} = \frac{\dot{Q}_o}{T_o} + \frac{\dot{Q}_{R,1}}{T_1} + \frac{\dot{Q}_{R,2}}{T_2} + ... + \sum_{inlet} \dot{m}_i s_i - \sum_{exit} \dot{m}_i s_i + \dot{\sigma}_{c,v} \tag{16}$$

Multiplying Eq. (16) throughout with T_0 and eliminating $\dot{Q}_0$ between Eq. (15) and Eq. (16) gives

$$\frac{d(E_{c.v} - T_0 * S_{c.v})}{dt} = \sum \dot{Q}_{R,i}\left(1 - \frac{T_0}{T_i}\right) + \sum_{inlet} \dot{m}_i \psi_i - \sum_{exit} \dot{m}_i \psi_i - \dot{W}_{c,v} - \dot{I}_0 \tag{17}$$

Eq. (17) represents the generalized availability balance for a given control volume.
I_o in Eq. (17) is defined as the irreversibility of the system given by $I_0 = T_0 * \sigma_{c,v}$. ψ_i is called the availability or exergy of the species *i* and is given by $\psi_i = e_i - T_0 s_i$.

Availability is the measure of work potential of energy [5]. Also called exergy, it is the measure of maximum work that can be extracted from a state point to the dead state (ambient temperature and pressure).

The work that can be extracted from a thermodynamic system is calculated using Eq. (17). This approach is called the availability analysis of the system. Availability analysis is conducted on a system to monitor work potential and work loss through a system when working fluids undergo change of state. Optimum work is defined as the work extracted from the control volume when the irreversibility is reduced to zero. Eq. (17) can be re-written for expressing optimum work as

$$\dot{W}_{c.v,\,opt} = -\frac{d(E_{c,v} - T_o * S_{c,v})}{dt} + \sum \dot{Q}_{R,i}\left(1 - \frac{T_o}{T_i}\right) + \sum_{inlet} \dot{m}_i \psi_i - \sum_{exit} \dot{m}_i \psi_i \tag{18}$$

One can either use the concept of lost work (using Eq. (17)) or use the entropy balance in Eq. (5) to find the rate of entropy generation ($\dot{\sigma}_{c,v}$). Lost work is found using the difference in optimum and actual work. Irreversibility rate or the rate of lost work is defined by

$$\dot{I} = \dot{W}_{c.v,\,opt} - \dot{W}_{c.v} = T_o * \dot{\sigma}_{c.v} \tag{19}$$

Further, the availability efficiency for the fuel cell is defined as

$$\eta_{avail} = \frac{W_{elec}}{|\Delta G_R|} \tag{20}$$

where W_{elec} is the actual work produced and ΔG_R is the work that can produced in an ideal fuel cell

Ideal Work Extraction from Products of Combustion

When a fuel is burnt, chemical energy is converted to thermal energy (more random energy). This conversion is an irreversible process and hence involves lost work. Under conditions of constant enthalpy (H) and pressure (P) (an adiabatic combustor), the products of chemical reaction leave at what is called the adiabatic flame temperature (T_{ad}). All thermal energy available at higher temperature products cannot be converted to work even when using a reversible heat engine as the energy conversion is limited by the second law.

In order to maintain reversibility between varying temperature reservoir and heat engine, one can employ a series of heat engines operating at very close temperatures [6]. Fig. (3) shows such a scheme where heat from products of adiabatic combustion (at adiabatic flame temperature) is converted to heat from a series of Carnot engines running at close temperature intervals. The hot products at T_{ad} are passed into a chamber (CV-1 in Fig. (3)). Transfer of heat cools the products and the temperature of products falls as they flow through the chamber till they reach a temperature T_0. The liberated thermal energy from products is transferred to a TER maintained at the same temperature. Heat transfer in the absence of a temperature gradient eliminates thermal irreversibility. Use of the process in Fig. 3 not only extracts the maximum possible work from hot products but also makes the process reversible.

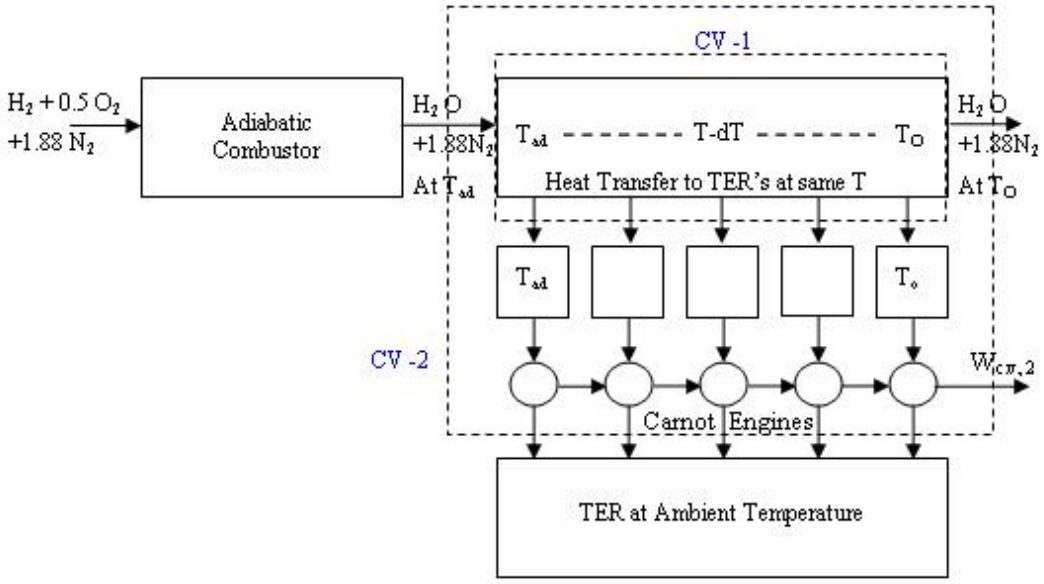

Fig. 3: Extraction of maximum reversible work following an adiabatic combustion reaction.

Consider CV-2 in Fig. 3. CV-2 includes CV-1 and all heat engines that extract work. The input for CV-2 is H_2O and N_2 at T_{ad} and the exit species are H_2O and N_2 at T_0. Work extracted is calculated using the availability balance over CV-2 (in Fig. 3). In Eq. (17), LHS is dropped for assumed steady state conditions. There is no heat transfer from reservoirs over the entire control boundary and $\dot{Q}_R$ is eliminated. As there is no thermal irreversibility and all Carnot engines in CV-2 are completely reversible, the total irreversibility of CV-2 is taken to be zero. The availability equation of Eq (17) reduces to $\dot{W}_{c.v} = \sum_{inlet} \dot{m}_i \psi_i - \sum_{exit} \dot{m}_i \psi_i$ which is the optimum work for given boundary. The work extracted from CV-2 is computed as 175,180 kJ per kmole of fuel burnt.

The chemical reaction which takes place in the adiabatic combustor is irreversible which leads to entropy generation. The optimum work that could be generated in the reactor is again given by the availability balance. It is computed as 48,159 kJ per kmole of fuel burnt for H_2 combustion with stoichiometric air mixture. As there is no work transfer

from the adiabatic reactor, Eq. (19) gives the entropy generation in the combustor to be 162 kJ per °K per kmole of fuel that is burnt. Overall system efficiency is calculated at 72.4% for the system with reactants H_2-O_2 entering at T_o and product H_2O exiting at T_o. Appendix I can be referred to for detailed calculations.

Availability balance considering whole of Fig. 3 gives an optimum work of 223,339 kJ per kmole of fuel burnt. Taking the ratio of work extracted to optimum work over the whole system computes the availability efficiency (η_{avail}) at 78%.

The set of series of Carnot engines running at various temperatures (in Fig. 3) can be substituted by a single Carnot engine to get the same overall system efficiency calculated above. The temperature at which heat should be transferred to the engine can be computed from previous analysis. Eq. (3), for efficiency (η) of 0.724 gives a T equal to 1080.15°K. This temperature is defined as the equivalent Carnot temperature ($T_{C,\,B}$). A single Carnot engine can replace the series of engines in Fig. 3 with the higher temperature thermal reservoir end maintained at 1080.15°K. This single Carnot engine is represented in Fig. 4.

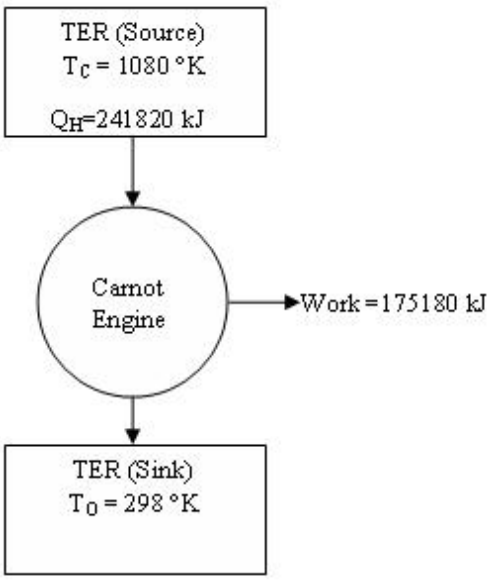

Fig. 4. Schematic of equivalent Carnot temperature.

Chemical and Mixing Irreversibility

When chemical reactions are involved in a system, in addition to thermal irreversibility, chemical and mixing irreversibilities also exist. When a set of inert (non-reacting) gases at the same pressure and temperature are introduced into an enclosure maintained at a temperature and pressure, they exert respective partial pressures according to their molecular composition. The change in pressure due to mixing causes mixing irreversibility. Further, if the gases react, they combine to form an equilibrium composition (if enclosure is maintained at the same temperature and pressure indefinitely). The change in composition due to chemical reaction causes chemical irreversibility. An effort to minimize these requires the condition $\delta\sigma \approx 0$. This means that the system should always operate close to equilibrium condition.

Chemical Equilibrium

A chemical reactor maintained at a certain temperature and pressure for a given input atoms of each species leads to only one equilibrium composition when a certain equilibrium reaction is assumed. Solution starts with atom balance equations for given species of atoms. Remaining equations are formed from the equilibrium constants at that temperature for assumed equilibrium reactions. The equilibrium composition will be same for two different combinations of input moles if the total atoms of each species remain the same in both cases [7]. An example for input mixture is 1 kmole of H2 and 0.5 kmole of O_2 which is the reactant mixture for fuel cell. This mixture would yield the same composition as 0.5 kmole of H_2, 0.25 kmole of O_2 and 0.5 kmole of H_2O. Observe that both compositions have 2 kmole atoms of Hydrogen, 1 kmole atoms of Oxygen.

Lutz Scheme for Extraction of Work

Lutz et al. [1] proposed that the efficiency of an ideal heat engine cannot be very different from the thermodynamic efficiency of a fuel cell when both processes are governed by the same overall reaction. They modeled an isothermal and isobaric chemical reactor coupled with heat engine to extract work. Fig. 5 describes the model. Their model uses the heat liberated from the combustion of hydrogen fuel (which is the same input to the fuel cell) to drive an ideal Carnot engine to extract mechanical work. Heat is rejected to a lower temperature reservoir (heat sink) at ambience. To reduce thermal irreversibility, the higher temperature end of the Carnot engine is maintained at the same temperature as that of the reactor.

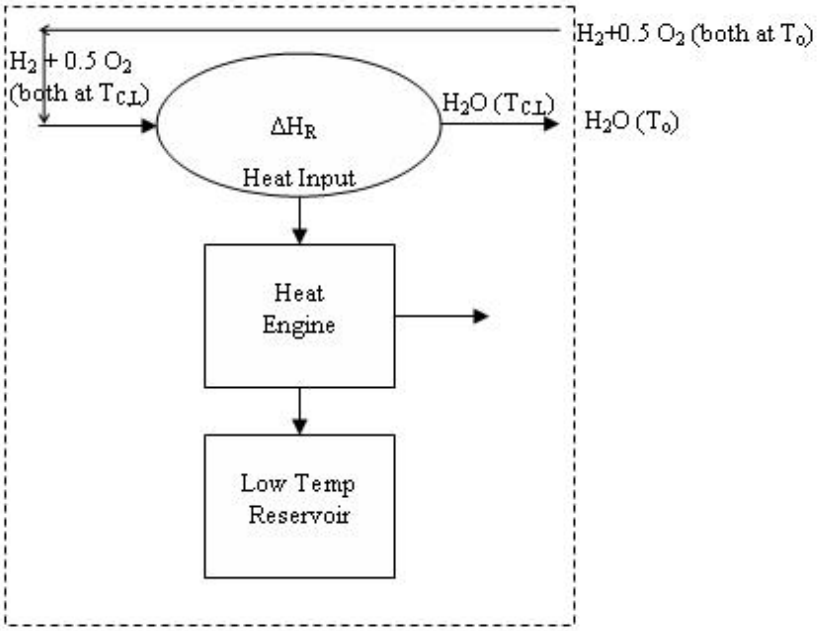

Fig. 5. Lutz et al. [1] model for finding ideal heat engine efficiency.

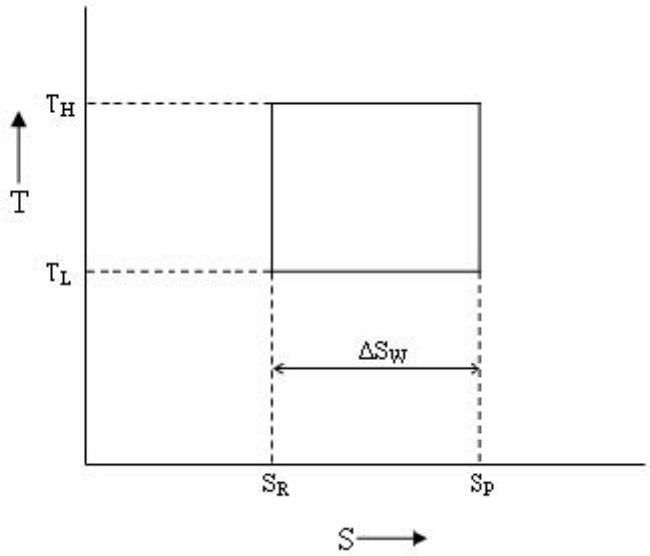

Fig. 6. T-S plot for heat engine in Lutz et al. [1] hypothesis.

The maximum temperature that the reactor can maintain is the maximum efficiency that the system can achieve. Lutz et al. [1] have defined the maximum temperature as the temperature of combustion ($T_{C,L}$) and proposed that this is achieved when the change in Gibbs free energy of the reaction ($\Delta G°_R$) goes to zero. $\Delta°G_R = G°_{prod} - G°_{Reac}$. Further, $\Delta G_R = (H_{Prod} - T*S_{Prod}) - (H_{Reac} - T*S_{Reac})$. Rearranging the terms and grouping enthalpies and entropies together, $\Delta G_R = \Delta H_R - T*\Delta S_R$. To obtain T_C, ΔG_R is equated to zero. This gives the expression

$$T_{C,L} = \left.\frac{\Delta H_R}{\Delta S_R}\right|_{T_C} \tag{21}$$

where $\Delta H_R < 0$ and $\Delta S_R < 0$. ΔS_R must not be confused with ΔS_W (in Fig. 6), change in entropy of the working fluid which does not undergo any chemical change.
As it can be seen, Eq. (21) needs to be solved iteratively to get the value for T_C.

This is the primary assumption made by Lutz et al. [1] It is assumed that complete combustion takes place at $T_{C,L}$ and pressure of 1 bar and that the reactor is isothermal. To assume reversibility, the model proposes that reactants enter at $T_{C,L}$ and products leave at $T_{C,L}$. The energy required to raise the reactants to this temperature is provided by the hot

gaseous products leaving the reactor and supplemental heating. For a control volume enclosing reactants and products at ambient temperature (dashed boundary in Fig. 5), it is shown that heat supplied to the overall process is the same as in the case of a fuel cell with reactants entering at T_0 and products leaving at T_0.

Consider the reaction in a fuel cell where 1 kmole of H_2 reacts with 0.5 kmole of O_2 and 2 kmole of N_2 to produce 1 kmole of H_2O and 2 kmole of N_2. $T_{C,L}$ for the reaction is computed at 3584°K (using Eq. (21)). Using $T_{C,L}$ the efficiency for the Lutz model is calculated. For $T = T_{C,L} = 3584$°K and $T_o = 300$°K, Eq. (3) yields an ideal fuel cell efficiency of 93.5%. Lutz et al. used this result to conclude that the efficiency of an ideal heat engine cannot be very different from that of a fuel cell.

The primary objection to this assumption is the complete combustion of fuel to products at $T_{C,L}$ or 3584°K. Change in Gibbs energy of the composition as the reactant is consumed (for a fixed temperature) can be plotted [8].

As the reaction proceeds, H_2 and O_2 are consumed and H_2O is formed, N_2 being the inert species. If the fixed mass of 74 kg (*1+0.5*32+2*28) is followed, there is a change in composition and hence the partial pressures for each species keeps changing. The Gibbs energy for a mixture G is computed using the equation

$$G = \sum_k N_k \overline{g}_k(T, p_k) \tag{22}$$

For the fixed mass, G decreases progressively due to chemical irreversibility. For a chemical reaction to occur in the forward direction, the chemical potential (or the Gibbs energy) of the reactants must be greater than that of the products. This imposes a condition $dG_{T,P} \le 0$. The product and reactant Gibbs energies are calculated using Eq. (22). For the equilibrium reaction $H_2 + 0.5O_2 \Leftrightarrow H_2O$, $dG_{T,P} = 0$ at given T and P means

that both directions for the reaction are equally favored and if a small amount of reactant is consumed, an equivalent amount of product is dissociated so that particular reactant and product composition is always maintained. The condition $dG_{T,P} < 0$ implies that the forward reaction is favored (more H_2O) is formed. In case $dG_{T,P} > 0$, the reverse direction (or dissociation of H_2O) is favored.

Fig. 7 shows the Gibbs energy of mixture for reaction progress at $T_{C,L}$ = 3584°K (isothermal and isobaric conditions). It can be seen that *G* reduces until approximately 0.59 kmole of H_2O are formed. Beyond this composition, *G* increases progressively. Minimum G is attained for the mixture when $dG_{T,P} = 0$. The composition when $dG_{T,P} = 0$ represents the equilibrium composition for the given input atoms and conditions of *T* and *P*. It can be seen that the branch left to the equilibrium composition satisfies the condition $dG_{T,P} \leq 0$. The other branch (to the right) has the condition $dG_{T,P} > 0$. As discussed above, for consumption of H_2, i.e., for the forward reaction to take place $dG_{T,P} < 0$. Hence, more amount of H_2 cannot be reacted beyond the equilibrium point and the branch to its right is impossible. So, a maximum of 0.61 kmoles of products are formed at this temperature. The assumption of complete combustion at this temperature is thus a violation of the second law of thermodynamics.

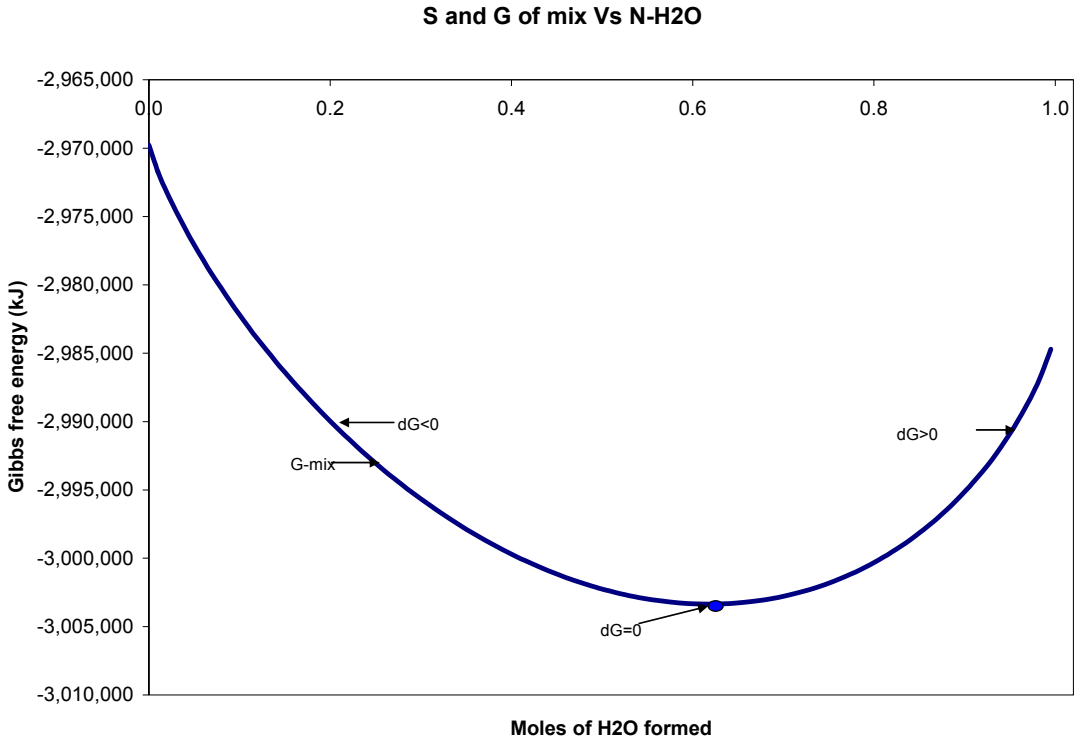

Fig. 7. Gibbs energy of mixture for isothermal hydrogen combustion at 3584°K.

Further, the calculation of heat supplied to the Carnot engine (using Eq. (4) where W = 0) is not valid due to incomplete combustion. As can be seen from Fig. 7, the *G* of pure reactants (*G* when kmole of H_2O is zero) and G of products (G when kmole of H_2O equals one) are also not equal for this temperature. This means $\Delta G_R \neq 0$.

Lutz et al. [1] assumed that ΔH_R and ΔS_R changes are very little at different temperatures, i.e., $\Delta H_R(T_{C,L}) \approx \Delta H_R(T_o)$ and $\Delta S_R(T_{C,L}) \approx \Delta S_R(T_o)$ giving $T_{C,L} = \dfrac{\Delta H(T_{C,L})}{\Delta S(T_{C,L})} \simeq \dfrac{\Delta H(T_o)}{\Delta S(T_o)}$.

This assumption was based on complete combustion. The increase in enthalpy of reactants and products is fairly linear with change in temperature (for assumption of complete combustion). This leads to an almost constant enthalpy of the reaction (ΔH_R)

for a wide range of temperatures. This is incorrect when enthalpy is calculated based on equilibrium composition. Similar is the assumption with entropy.

The other assumption in their analysis is the equal changes in entropy for reactor (ΔS_R) and working fluid in the Carnot engine (ΔS_W. Refer Fig. 6). The reactor is not a thermal energy reservoir as it involves a chemical reaction which is inherently irreversible. Using Eq. (7) in a steady state mole basis, we get $\Delta S_R = \frac{Q}{T_C} + \sigma$. Heat supplied by reactor is calculated using Eq. (4) for steady and no-work interaction for reactor. As work interactions are absent in the reactor, heat liberated is calculated as ΔH_R for every kmole of fuel burnt. This gives $\Delta S_R = \frac{\Delta H_R}{T_{C,L}} + \sigma$. All heat liberated in reactor is supplied to the Carnot engine. Since Carnot cycle is reversible, the change in entropy of working fluid is given by $\Delta S_W = \frac{\Delta H_R}{T_{C,L}}$. This follows that $\Delta S_R \neq \Delta S_W$. It shows that changes of entropy for the reactor and working fluid cannot be assumed the same.

Hassanzadeh and Mansour's Literature

On analysis of the work done by Lutz et al., Hassanzadeh and Mansouri from University of Kerman, Iran brought out their work based on equilibrium composition for different temperatures. In their paper, they acknowledge that fuel cells and heat engines are constrained by the second law.

Their primary objection to the Lutz model was to the assumption of complete combustion at high temperatures for H_2 and O_2 system. Discussion in the previous section shows incomplete combustion for the system at specified temperature.

Hassanzadeh et al. redefined the temperature of combustion to include the irreversibility in the combustion reaction. They defined $T_{C,H}$ as

$$T_{C,H} = \frac{-\Delta H_R\big|_{T_{C,H}}}{-\Delta S_R\big|_{T_{C,H}} + \Delta S_{gen}} \tag{23}$$

Eq. (23) is valid for condition of $\Delta S_R < 0$ and $\Delta H_R < 0$. ΔS_{gen} is defined as the entropy generation due to combustion of H_2 fuel in an adiabatic combustor. And this is always a positive number because of the increase in entropy due to chemical irreversibility. This condition makes $T_{C,H} < T_{C,L}$. Hassanzadeh et al. used $T_{C,H}$ to find the temperature of the combustor (or higher temperature TER).

When 1 kmole of H_2 reacts with 0.5 kmole of O_2 and 2 kmole of N_2 to produce 1 kmole of H_2O and 2 kmole of N_2 (same reaction in Lutz scheme), $T_{C,H}$ is calculated as 1080°K. Computing the efficiency based on $T_{C,H}$ for this reaction drops the efficiency from 93.5% to 72.4%

Equivalent Carnot temperature is defined ($T_{C,B}$) for maximum work extraction followed by adiabatic combustion. $T_{C,B}$ represents the temperature at which maximum work can be extracted from hot gases. Refer Appendix II for derivation.

$$T_{C,B} = \frac{-\Delta H_R\big|_{T_0}}{-\Delta S_R\big|_{T_0} + \sigma_{ad}} \tag{24}$$

σ_{ad} represents entropy generation in adiabatic combustion (ΔS_{gen} in $T_{C,H}$). Eq. (23) and Eq. (24) yield almost the same result for the reaction specified above. This is because ΔH_R and ΔS_R for the reaction do not change from T_0 to $T_{C,H}$. It is to be noted that $T_{C,B}$ is based on products of adiabatic combustion while $T_{C,H}$ is calculated for an isothermal reactor.

OBJECTIVE

Lutz et al. [1] proposed that the efficiency of an ideal heat engine is close to that of a fuel cell when both processes have the same chemical reaction. Hassanzadeh refuted the assumptions in the Lutz model and stated that the efficiency of an ideal engine cannot compare with that of a fuel cell. The objective of this work is to determine if, there exits an ideal process that results in the same efficiency as that of a fuel cell (when both have the same reactants and products), and if so at what conditions.

Futuregen [9] is a new United States initiative to produce a zero-emission power plant. Gasification of coal gives Carbon monoxide (CO) and Ammonia (NH_3). The Futuregen process involves reaction of steam with the above gasification products to produce Carbon dioxide (CO_2) and Hydrogen (H_2). The oxidant (O_2) must also be supplied separately. CO_2 in the H_2-CO_2 mixture acts like the inert gas N_2 (if O_2 is obtained from air). Different coals give different H_2: CO_2 compositions. The other objective of this work is to determine the effect of the inert gas species and the composition of Futuregen products when supplied to the above process. This would allow the trade-off between the cost of inert gas removal and increase in efficiency.

MODELING

The primary objective of this work is to determine if an ideal process exists that can extract as much work from chemical reactants as a fuel cell can. This requires a process which minimizes chemical and thermal irreversibilities. This section covers the development of a process which makes the chemical reaction and work extraction as close to reversible as possible.

A numerical analysis on the process to find irreversibility is discussed. Further, availability balance used in calculation of work extraction for the process is explained. Finally, the sequence of the procedure is enumerated as a recap.

Hypothetical Scheme

The following paragraphs explain the chemical reaction and equilibrium compositions for different temperatures and how to make the chemical reaction reversible. Also noted is the effect of mixing irreversibility.

Consider a reactant composition of 1 kmole of H_2, 0.5 kmole of O_2 and 1.88 kmole of N_2 introduced into an isothermal chemical reactor maintained at 3584°K and a pressure 1 bar. The species will equilibrate to 0.54 kmole of H_2O, 0.46 kmole of H_2 and 0.23 kmole of O_2 with N_2 as the inert species. For the present case, $H_2 + 0.5O_2 \Leftrightarrow H_2O$ is the equilibrium reaction considered. As discussed in chapter 2.2.4 mixing and chemical irreversibilities occur in the above reactor. Introduction of the equilibrium composition (0.54 kmole of H_2O) will eliminate chemical irreversibility. Each species in the reactor exert partial pressures based on the equilibrium composition. So, if equilibrium moles of

species maintained at respective partial pressures are introduced to the reactor, it would have no mixing irreversibility. Due to absence of temperature gradient, thermal irreversibility is eliminated.

Fig. 8 is a plot for the G of reacting systems at different temperatures. The input reactants considered for different reactor temperatures is exactly the same and identical to reactants for reactor at 3584°K. It can be seen from Fig. 8 that for different temperature reactors, the mixture reaches a different composition for the condition dG=0. It must be remembered that the branch to the right of the point dG=0 is impossible and the reaction stops with attainment of the equilibrium composition. If equilibrium mixture from 3550°K reactor is fed to 3000°K reactor, a higher amount of H_2O formation is observed. Similarly if the mixture from 3550°K reactor is fed to 3600°K reactor, lesser H_2O is observed due to dissociation. When the next reactor is at a temperature close to the previous one, minimum *G* points for the mixture (where dG=0) lie very close to each other. If the temperature steps are brought very close to each other, it approaches an approximate reversible path. Theoretically, if an infinitesimal temperature difference is maintained between two reactors, the reaction can be made reversible. Using several chemical reactors at very close temperatures is proposed for eliminating chemical irreversibility in the proposed process.

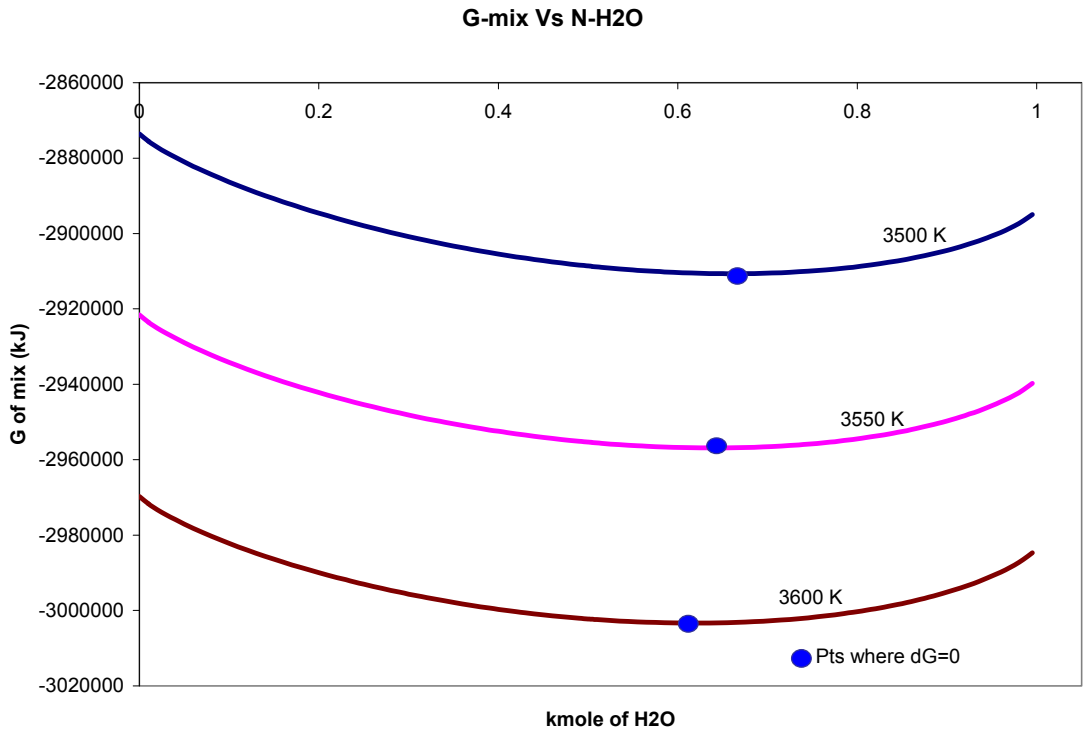

Fig. 8. Gibbs energy of mixture for different reaction temperatures.

Fig. 9 is a detailed sketch for the proposed scheme to make chemical reaction and work extraction reversible. It consists of two main parts. The left block of Fig. 9 is the inert system represented by control volume 1 (CV-1) and the block to the right is the reacting system indicated by control volume 2 (CV-2). CV-2 is where the chemical reaction and work extraction takes place. It contains a series of isothermal chemical reactors maintained at 1 bar pressure. Reactors are such that the adjoining reactor is at a slightly lower temperature compared to the preceding one when moving from left to right. Due to its comparison with the fuel cell, this process has the same input atoms as in a fuel cell operation i.e., 2 kmole of H atoms and 1 kmole of O atoms. 1kmole of O atoms obtained from the air will include 3.76 kmole of N atoms (as N_2/O_2 ratio on a mole basis in air is 3.76).

For CV-2, as the first reactor is at a maintained at 5000°K, the reactants entering must be at the equilibrium composition to avoid irreversibility. The equilibrium products obtained at this temperature and pressure of 1 bar are 0.88 kmole of H_2, 0.44 kmole of O_2, 0.12 kmole of H_2 and 1.88 kmole of N_2. To avoid mixing irreversibility, each of the reactants enters at partial pressures and heated to 5000°K. CV-1 is used for raising the temperature of the reactants from room temperature (298°K) to 5000°K. It employs a series of reversible heat pumps running at close temperature intervals. A heat pump is used to raise the temp of reactants from 298°K to a little higher temperature, say 299°K. This is followed by another heat pump which raises the temperature a little higher. Using a series of such pumps raises the reactants temp to 5000°K. This scheme is used to make the heat transfer to reactants completely reversible. If a single heat engine were to be used to raise the temperature of reactants, heat transfer would involve thermal irreversibility due to a very large temperature gradient. By facilitating heat transfer in small temperature fractions, temperature gradients are avoided, thus making the process reversible. A possible contention in raising the reactants to such high temperature could be that of molecular dissociation (splitting of H_2O into H_2 and O_2). A hypothetical anti-catalyst is assumed to prevent such dissociation of reactants at partial pressures. The left block in CV-1 represents this complete process. The work required to run the heat pumps is extracted from CV-2. The end of this process makes reactants ready to enter CV-2.

As mentioned, CV-2 extracts work by chemical reaction and thermal energy of reactants. As reactants are let into the first reactor at 5000°K (maintained at 1 bar), mixing occurs but no change in composition occurs because reactants are already at equilibrium composition. It is proposed that a fraction of the thermal energy is extracted and supplied to a Carnot engine to extract work. The higher temp reservoir for this engine is at 5000°K so that temperature gradients do not exist for heat transfer. This energy extraction slightly reduces the temperature of the reactants, say to 4999°K. The mixture at this temperature is fed into the next reactor which is maintained at 4999°K. Due to the

small change in temperature, the mixture reaches a new equilibrium as a fraction of H_2 reacts to form H_2O. Heat is liberated due to this combustion reaction. Similar to the earlier case a little energy is extracted from mixture to further reduce its temperature by a small fraction. As the reactor is maintained isothermal, energy is passed on to a Carnot heat engine operating at the temperature of the reservoir. The new mixture is passed onto the next reactor which is at that temperature and lets the mixture equilibrate to a new composition. The earlier steps are again repeated in small temperature intervals until the mixture reaches room temperature. By the time the mixture reaches the end of CV-2, at 298°K all of H_2 is combusted to products and mixture consists of 1 kmole of H_2 and 1.88 kmole of N_2. The mixture leaving CV-2 at ambient temperature shall be called the product mixture for CV-2.

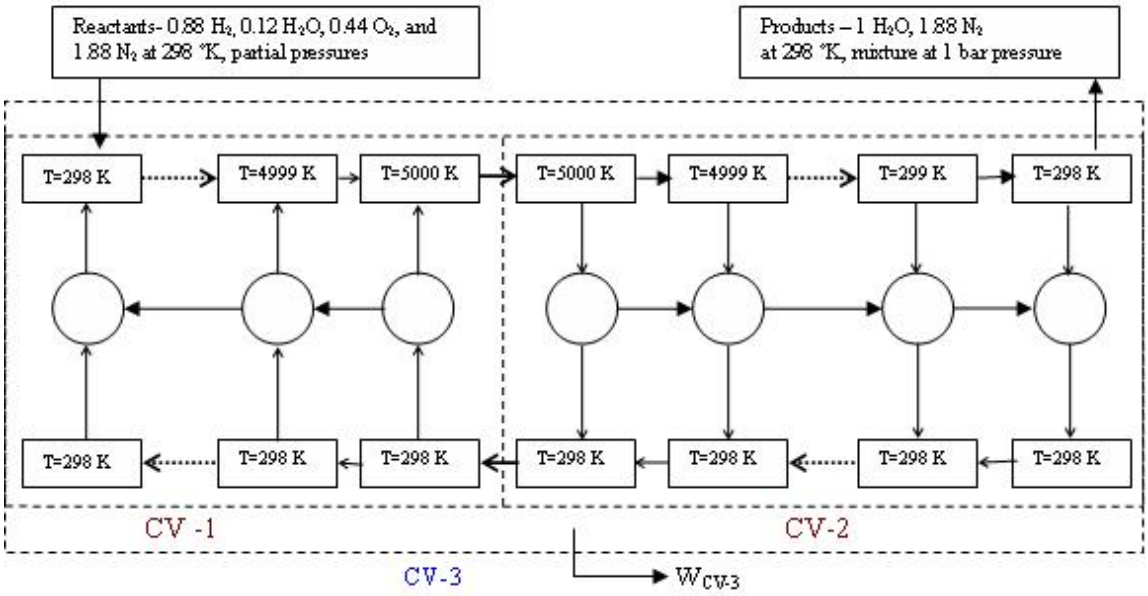

Fig. 9 Schematic representing proposed process for extraction of work from combustion reaction.

If a control boundary is assumed over the whole system combining both CV-1 and CV-2 making it a single control volume CV-3 as indicated in Fig. 9, the overall reaction for the system can be written as $0.88H_2 + 0.44O_2 + 0.12H_2O + 1.88N_2 \rightarrow H_2O + 1.88N_2$.

The system has a net production of 0.88 kmole of H_2O with work extraction and heat interaction with ambient at T_0. The equivalent reaction for the system is $H_2 + 0.5O_2 \rightarrow H_2O$. The input reactants and exiting products are at 298°K. This is the exact same reaction that drives a fuel cell with same reactant mixture at its inlet and products at the exit and which has heat interactions with the ambient and produces electric work.

Analysis of the Chemical Reactor- Heat Engine Model

Availability analysis is conducted over the whole process to calculate the maximum possible work extraction from the system. Eq. (17) which gives the availability balance requires the computation of the term *I*, which is the irreversibility for the process. The thermodynamic modeling for the whole process can be divided into analysis for individual reactors. Fig. 10 shows the schematic for reactor model that needs to be analyzed for entropy generation of the process. Each reactor-heat engine reservoir pair is maintained at the same temperature as explained in the previous section. After heat is transferred at the same temperature to the high temperature TER, work is extracted using a Carnot engine. As Carnot engine is principally reversible and heat transfer does not experience a gradient, these processes do not involve entropy generation. The remainder is the isothermal reactor where the reactants undergo reaction to reach chemical equilibrium. The dotted boundary is a generalized control volume which can be used for calculating the irreversibility of the chemical reaction in any of the reactors in CV-2.

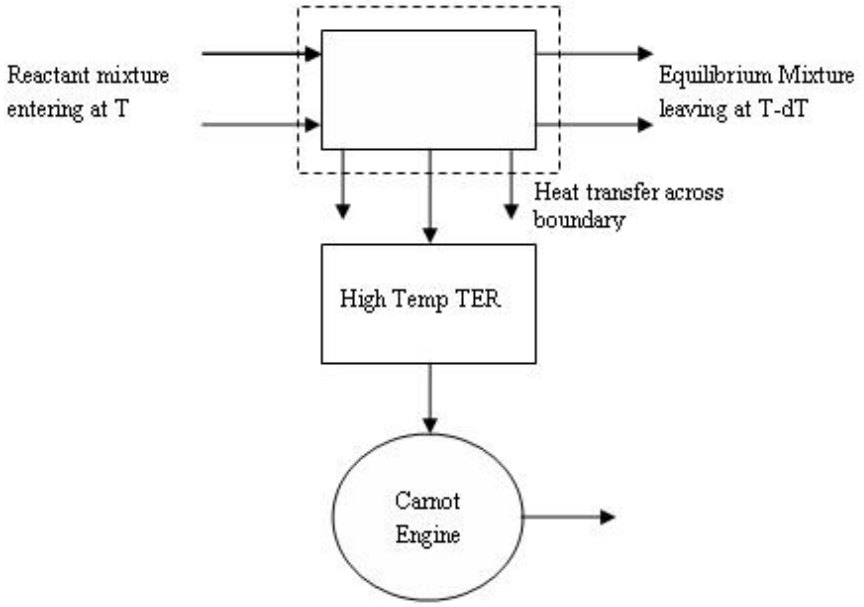

Fig. 10. Control volume considered for thermodynamic analysis of infinitesimal temperature change reactor-heat engine system.

The species composition entering and leaving each reactor must be calculated. The reactors are isothermal at a pressure maintained at 1 bar. So the product mixture leaving each reactor is the equilibrium composition for the given temp and pressure. This needs calculation of the equilibrium composition for each reactor (different temperatures). The system being considered has N_H kmole atoms of H, N_O kmole atoms of O and N_N kmole atoms of N.

$$N_H = 2N_{H_2} + 2N_{H_2O} \tag{25}$$

$$N_O = N_{H_2O} + 2N_{O_2} \tag{26}$$

$$N_N = 2N_{N_2} \tag{27}$$

But there are four unknowns (H_2, O_2, H_2O and N_2) that are in the product mixture. Atom balance gives three equations for H, O and N atoms. The fourth equation comes from consideration of the equilibrium composition at the given temperature and pressure. Equilibrium constant is defined as

$$K^\circ(T) = \exp\left(\frac{-\Delta G^\circ_R}{\bar{R}T}\right) \tag{28}$$

$\Delta G°_R$ is the Gibbs energy of reaction given by $\Delta G° = \Delta H° - T\Delta S°$ for the equilibrium reaction $H_2O \Leftrightarrow H_2 + 0.5O_2$ at the temperature T for a standard pressure of 1 bar.
Further

$$K°(T) = \frac{N_{H_2} * (N_{O_2})^{1/2}}{N_{H_2O}} * \left(\frac{P}{P°N}\right)^{1/2} \tag{29}$$

It must be noted that N in Eq (29) represents the total moles ($N_{H_2} + N_{O_2} + N_{H_2O} + N_{N_2}$) in mixture at specified temperature.

Clubbing Eq. (29) to the three atom balance equations (Eqs. (25),(26) and (27)) gives a set of four equations with four unknowns. If all the unknowns above are expressed in terms of N_{O_2}, the derivation of the solution for N_{O_2} yields a cubic equation of the form

$$a_3 N_{O_2}^3 + a_2 N_{O_2}^2 + a_1 N_{O_2} + a_0 = 0 \tag{30}$$

The detailed derivation of the equation and the expressions for coefficients a_1, a_2, a_3 and a_4 can be found in Appendix III. It must be noted that when $a_3 \to 0$, Eq. (30) reduces to a quadratic equation. The MS EXCEL program formatted to calculate the equilibrium composition computes solutions for both cubic and quadratic cases and assigns the solution to N_{O_2} according to the coefficients a_3 and a_2. The program uses Manual of Mathematics by Granino Korn and Theresa Korn [10] to calculate the explicit roots of the cubic equation.

The following description is the use of thermodynamic equations to calculate the irreversibility of the process.

For the boundary considered in Fig. 10, the reactant mixture enters at a temperature T and is allowed to reach to reach an equilibrium composition at a slightly lower temperature 'T-dT'. As explained in the modeling section, the equilibrium mixture leaves at a slightly lower temperature, say T-dT. It is to be noted that the mixture entering the volume and that leaving are different. Eq. (2) applied to the control volume for steady state and zero work transfer over a short period of time gives

$$\delta Q = H\big|_{T-dT,Nk+dN\kappa} - H\big|_{T,Nk} = dH_{P-R} \tag{31}$$

Applying Eq (3) for the same boundary gives

$$\frac{\delta Q}{T} + S\big|_{T,Nk} - S\big|_{T-dT,Nk+dNk} + \delta\sigma_{C.V} = \frac{\delta Q}{T} + dS_{R-P} + \delta\sigma_{C.V} = 0 \tag{32}$$

Eliminating δQ from Eq. (31) and Eq. (32) gives

$$T\delta\sigma_{C.V} = -dH_{P-R} + TdS_{P-R} \tag{33}$$

The irreversibility due to "dT" across the infinitesimal reactor can be computed. Then one can sum up this value over all the reactors:

$$I = \int T\delta\sigma_{C.V} = -\left(H\big|_{\mathrm{Pr}od,298} - H\big|_{\mathrm{Re}ac,5000^\circ K}\right) + \int TdS_{P-R} \tag{34}$$

Further adding and subtracting the term SdT to eq (33) gives

$$T\delta\sigma_{C.V} = -dH_{P-R} + d(TdS) - SdT = -dG_{P-R} - SdT_{P-R}\,.$$

Taking the integral over the cycle

$$I = \int T\delta\sigma_{C.V} = -\left(G\big|_{\mathrm{Pr}od,298} - G\big|_{\mathrm{Re}ac,5000^\circ K}\right) - \int SdT \tag{35}$$

Eq (34) gives an alternative expression for eq (35) to calculate the irreversibility for the whole process.

Remember that Gibbs property for any species can be calculated using Eq (7)

Note that

$$H = \sum N_k(T,P)\bar{h}_k(T) \tag{36}$$

$$S = \sum N_k(T,P)\bar{s}_k(T,p_k) \tag{37}$$

The enthalpy of any species 'k' can be found using the equation

$$\bar{h}_k(T) = \bar{h}_{f,298^\circ K} + \bar{h}_{k,t}(T) \tag{38}$$

As can be seen from Eq (38), enthalpy of any species at elevated temperatures consists of two parts. $\bar{h}_{f,298^\circ K}$ is the enthalpy of formation for a molecule and is the energy required to form that molecule from its basic elements at that temperature. The enthalpy of formation for pure elements occurring in natural form is zero. Examples of naturally occurring elements are H_2 and O_2. $\bar{h}_{k,t}(T)$, called thermal enthalpy is attributed to thermal energy alone. It can be found using the equation:

$$\overline{h}_{k,t}(T) = \int_{298}^{T} \overline{C}_{p,k}(T)dT \tag{39}$$

The entropy of the species in a mixture (existing at partial pressure) is given by

$$\overline{s}_k(T, p_k) = \overline{s}^{\circ}{}_k(T) - \overline{R}\ln(p_k) = \overline{s}^{\circ}{}_k(T) - \overline{R}\ln(\frac{X_k P}{P^0}) \tag{40}$$

$\overline{s}^{\circ}{}_k(T)$ represents the absolute entropy of the species existing at a pressure of 1 bar and $\overline{R}\ln(p_k)$ is the pressure correction for species which exists at partial pressure in a mixture. X_k in Eq. (40) is the mole fraction of species in the mixture. The absolute entropy at any temperature is calculated using

$$\overline{s}^{\circ}{}_k(T) = \overline{s}^{\circ}{}_{k,298}(T) + \overline{s}^{\circ}{}_{k,t}(T) \tag{41}$$

$\overline{s}^{\circ}{}_{k,f}(T)$ is the species reference entropy at ambient temperature and $\overline{s}^{\circ}{}_{k,t}(T)$ is thermal part given by

$$\overline{s}^{\circ}{}_{k,t}(T) = \int_{298}^{T} \frac{\overline{C}_{p,k}(T)}{T} dT \tag{42}$$

Availability Balance for the Hypothetical Scheme

If irreversibility for the hypothetical scheme is computed, the work extraction in CV-2 of Fig. 9 can be calculated using Eq. (17). Steady state considered for the system eliminates the first term in RHS of Eq (17). There is no heat transfer from out side the boundary and the second term of RHS also gets eliminated. Eq (17) reduces to

$$W_{cv-2} = \sum_{5000^\circ K}^{Reac} N_k \psi_k - \sum_{298^\circ K}^{Prod} N_k \psi_k - I \tag{43}$$

Inlet to CV-2 (or) the reactant composition is 0.88 kmole of H_2, 0.44 kmole of O_2, 0.12 kmole of H_2O and 1.88 kmole of N_2 at a temperature of 5000°K. The products leaving CV-2 are 1 kmole of H_2O and 1.88 kmole of N_2.

CV-1 in Fig. 9 uses a series of reversible heat engines operating at small temperature intervals to heat the reactants which serve as input to CV-2. Availability analysis on CV-

1 determines the amount of work that needs to be supplied to CV-1 to raise the temperature of reactants from 298°K to 5000°K. It must be noted that the process in CV-1 is completely reversible and hence *I* is zero. Steady state assumption applied to CV-1 drops LHS of Eq (17). There is no heat transfer to CV-1 from outside the control boundary. This drops the first term on RHS of Eq. (17). The availability balance on CV-1 yields

$$W_{cv-1} = W_{cv,\,opt} = \sum_{298°K}^{Reac} N_k \psi_k - \sum_{5000°K}^{Reac} N_k \psi_k \tag{44}$$

Inlet to CV-1 or the reactant composition is 0.88 kmole of H_2, 0.44 kmole of O_2, 0.12 kmole of H_2O and 1.88 kmole of N_2 at a temperature of 298°K. The exit composition is the same at a temperature of 5000°K. Due to higher temperature of the same composition, availability at exit is higher and $W_{cv\text{-}1}$ computes to a negative value indicating work supplied. The sum of both works gives the net work output from the whole system which is compared to work extracted from fuel cell.

$$W_{CV\text{-}3}=W_{CV\text{-}1}+W_{CV\text{-}2} \tag{45}$$

Procedure

1. Assume that $N_H = 2$, $N_O = 1$ and $N_N = 3.76$ as atoms entering the reactor.
2. Curve fit C_P data for required species. NIST [11] tabulates the specific heat data for numerous chemical species for a various temperatures till 5000°K. A fifth degree polynomial is curve fitted for data so that calculation of specific heat for any reactant at any temperature can be substituting that temperature in the polynomial equation. The equation will be of the form

$$C_p = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5 \tag{46}$$

The coefficients for the composition considered can be found in Table 1.

Table 1
Curve fitted coefficients for specific heat of species.

Species	$\bar{h}_{f,298}$ kJ/kmol	$\bar{s}^{o}_{298}$ kJ/kmol K	a_0	a_1	a_2	a_3	a_4	a_5
H_2	0	130.57	29.14	-2.551e-3	5.601e-6	-2.142e-9	3.466e-13	-2.064e-17
O_2	0	0	25.34	1.592e-2	-9.052e-6	2.923e-9	-4.65e-13	2.867e-17
H_2O	-241820	188.72	30.93	5.496e-3	9.139e-6	-5.200e-9	1.040e-12	-7.286e-17
N_2	0	191.5	27.78	3.000e-3	3.876e-6	-2.660e-9	5.943e-13	-4.508e-17
CO_2	-393520	213.69	22.53	5.974e-2	-3.868e-5	1.271e-8	2.045e-12	1.279e-16

3. Compute $\bar{h}_k^{o}(T) = \bar{h}^{\circ}_{f,k} + \int_{298}^{T} C_{p,k}(T)dT$ for H_2, O_2 and H_2O.

4. Compute $\bar{s}_k^{o}(T) = \bar{s}^{\circ}_{k,298} + \int_{298}^{T} \frac{C_{p,k}}{T}dT$ for H_2, O_2 and H_2O.

5. Compute $\bar{g}_k^{o}(T) = \bar{h}^{\circ}_k(T) - T\bar{s}^{\circ}_k(T)$ for H_2, O_2 and H_2O.

6. Calculate K°(T) for the equilibrium reaction $H_2O \Leftrightarrow H_2 + 0.5O_2$ using Eq. (40). Note here that ΔG°_R is calculated as

$$\Delta G_R^{\circ}(T) = \bar{g}_{H_2}^{\circ}(T, p_k) + \bar{g}_{O_2}^{\circ}(T, p_k) - \bar{g}_{H_2O}^{\circ}(T, p_k) .$$

K°(T) can also be calculated using the based out of the JANAF tables, NSRDS-NBS-37, 1971. Equilibrium constants for common equilibrium reactions are tabulated for various temperatures. One may construct a linear curve fit expression for K° (T) ($Log_{10}K^{\circ}(T) = A - B/T$) as the fourth equation for solving the composition.

The use of Eq. (28) for computing K°(T) is consistent as curve fitted data for C_P of each species is used in calculation of G and hence in the calculation of ΔG_R for each temperature step.

7. Use Eq (30) to calculate N_{O_2}, or the kmole of O_2 in equilibrium mixture. Once N_{O_2} is calculated, the equilibrium composition is determined. Equations for other species in

terms of N_{O_2} are given in Appendix III. Solution for quadratic equation is assigned in case $a_3 \to 0$. Else solution for the cubic case is retained.

8. Calculate $\bar{h}_k(T)$ for each equilibrium species at temperature T using Eq (39).

9. Calculate $\bar{s}_k(T, p_k)$ for each equilibrium species at temperature T using Eq (40).

10. Calculate $\bar{g}_k(T, p_k)$ for each equilibrium species at temperature T using Eq (7).

11. Compute G of the equilibrium mixture using Eq (22).

12. Compute H of the equilibrium mixture using Eq (36).

13. Compute S of the equilibrium mixture using Eq (37).

14. Repeat steps 1 through 13 by changing T to 'T-dT', 'T-2dT' and so on till temperature step reaches ambience (298°K).

15. Calculate $\delta\sigma_{C.V}$ for each step using Eq (33) and irreversibility (I) for the whole process using Eq (35).

In Eq (33), $dG = G_{prod} - G_{reac}$ and S in SdT is the average entropy of the reactant and product mixtures where dT is the temperature interval step for the series. In Eq (35) $\int SdT$ is the sum of SdT obtained for all temperature steps from 5000°K to 298°K.

16. Results from Step 15 can be used in availability balance of Eqs (43) and (44) to find out W_{CV-1} and W_{CV-2}.

Analysis is completed by finding the overall work extracted (W_{CV-3} from Eq (45)) from the hypothetical thermal energy conversion process and comparing it to the work extracted by a fuel cell for identical reactant and product conditions.

RESULTS AND DISCUSSION

This section explains the results obtained from numerical analysis on the hypothetical process. The trend of equilibrium composition with change reactor temperature will be explained. The irreversibility for the process as a function of the temperature step size will also be discussed.

The results of parametric study on change of inert composition are also explained. The effect of change in the system pressure is also noted. The proposed scheme for other fuels is also discussed.

Equilibrium Composition

Fig. 11 is the plot of No_2 (or the kmoles of O_2 in equilibrium mixture) formed at various isothermal reactors for a temperature range of 5000°K to 500°K. Consistent with the discussion in the literature review section, for the H_2 and O_2 system, more H_2O is formed at lower temperatures. At 5000°K, approximately 0.12 moles of H_2O exist. H_2O formation is steady till about a temperature of 3700°K and from then rapidly increases till about a temperature of 1670°K where 99.99% of the H_2 is completely converted to its products. It can be observed from Fig. 11 that below 1700°K, moles of H_2O are seen to be constant at around 1 kmole. This means little change in equilibrium composition below 1700°K. The computation in the excel program is performed till a lower temperature of 500°K. This limit is because MS EXCEL has a computation power of up to 15 decimals and the change in moles of H_2O formed below 500°K is beyond this accuracy. And the results obtained at 500°K are reasonably close to the ones at ambient temperature of 298°K.

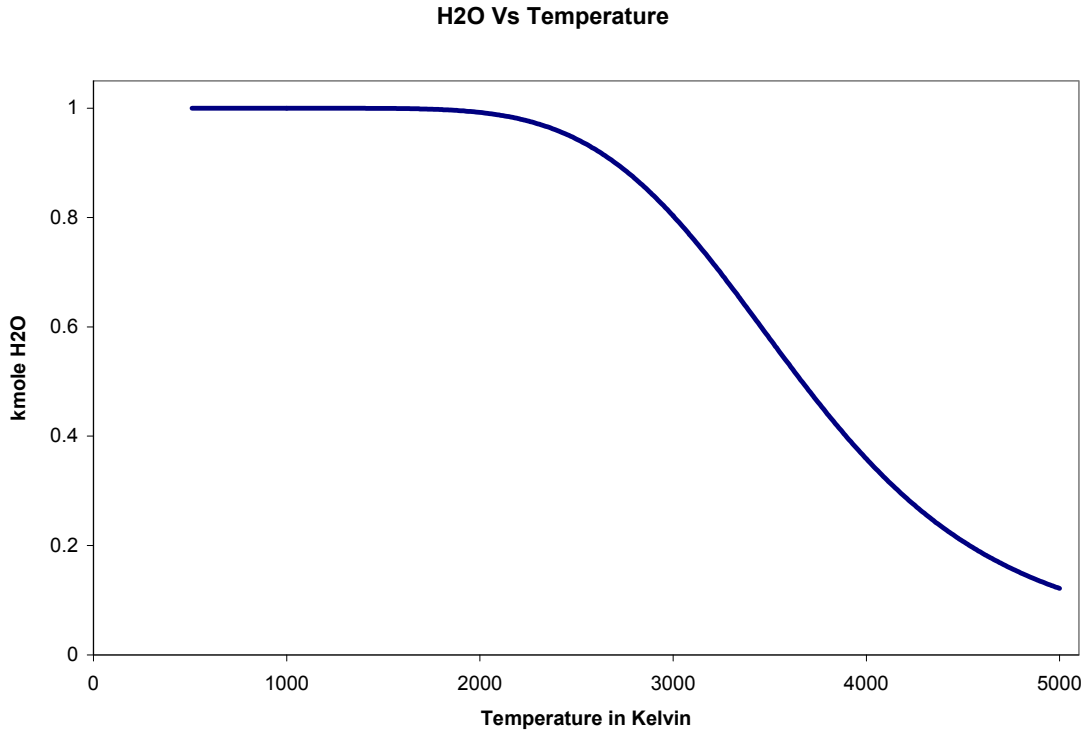

Figure 11: Formation of H_2O at different isothermal reactor temperatures.

Fig. 12 is a plot of the *G* and *S* for the reactant mixture as it passes through the various isothermal reactors. A good way to understand this is to follow a fixed mass system of reactants entering the first reactor at 5000°K till the mixture reaches 500°K while *G* and *S* are tracked as equilibrium mixture leaves each reactor. As the temperature of the reactor decreases, more amount of H_2O is formed. This changes the partial pressure of each species. Heat transfer from the reactors decreases the entropy with decrease in temperature. *G* of the mixture increases with decrease in the temperature. On observing the Gibbs function as $G = H - TS$, *H* and *S* decrease with decrease in temperature. But the decrease in product *TS* for each species is significantly higher when compared to decrease in *H*. Thus we find an increase in the Gibbs energy of the mixture. It can be seen from Fig. 12 that the Gibbs function is a smooth curve while the Entropy of mixture does not have a linear fit.

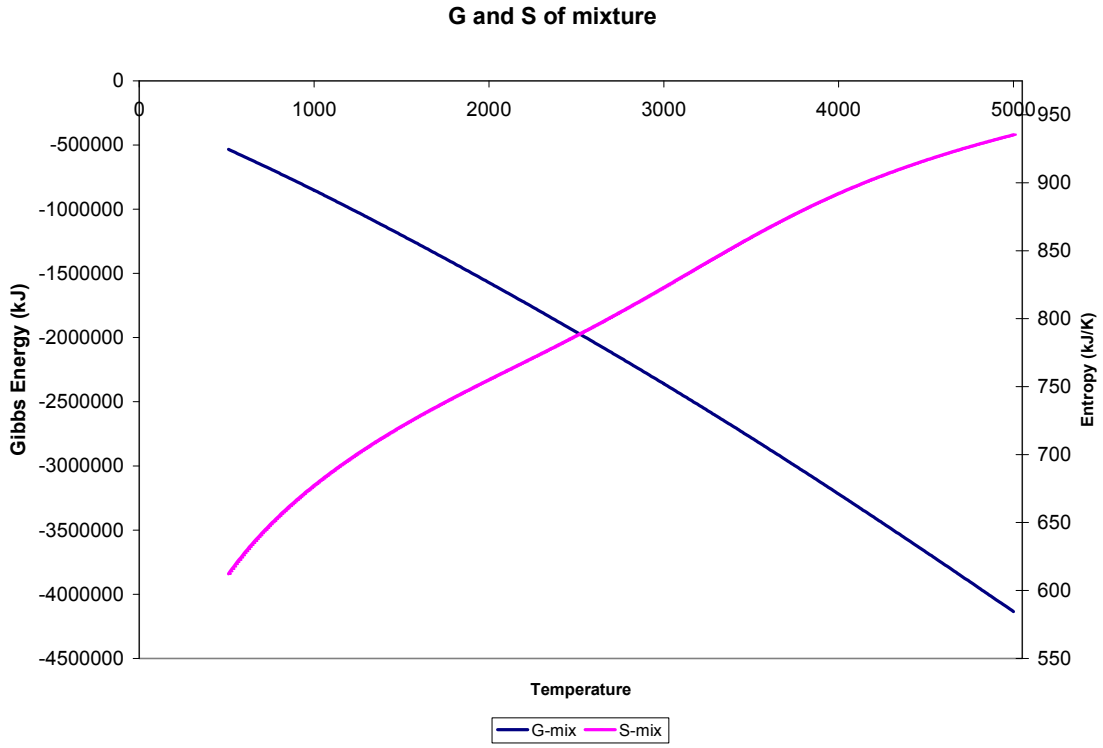

Figure 12: Plot of G and S of the mixture at different temperatures.

Irreversibility of the Ideal Process

Fig. 13 is a plot for the total irreversibility of the system as a function of the temperature step size (temperature difference between two consecutive reactors). The integral $\int sdT$ is in Eq. (35) is evaluated using both Simpson's rule and trapezoidal rule for numerical integration. The blue line is Fig. 13 for total irreversibility of process when the integral is based on trapezoidal rule. At large temperature intervals a small negative result is observed for the process. It is seen that the total irreversibility approaches zero for a small temperature step size. Irreversibility based on Simpson's rule is also shown in the same plot and can be seen close to zero when compared to the trapezoidal rule. The integral obtained from Simpson's rule is more accurate when compared to the one from trapezoidal rule because it uses a three point fit for polynomial equation to calculate the integral as against a two point linear fit in the trapezoidal rule.

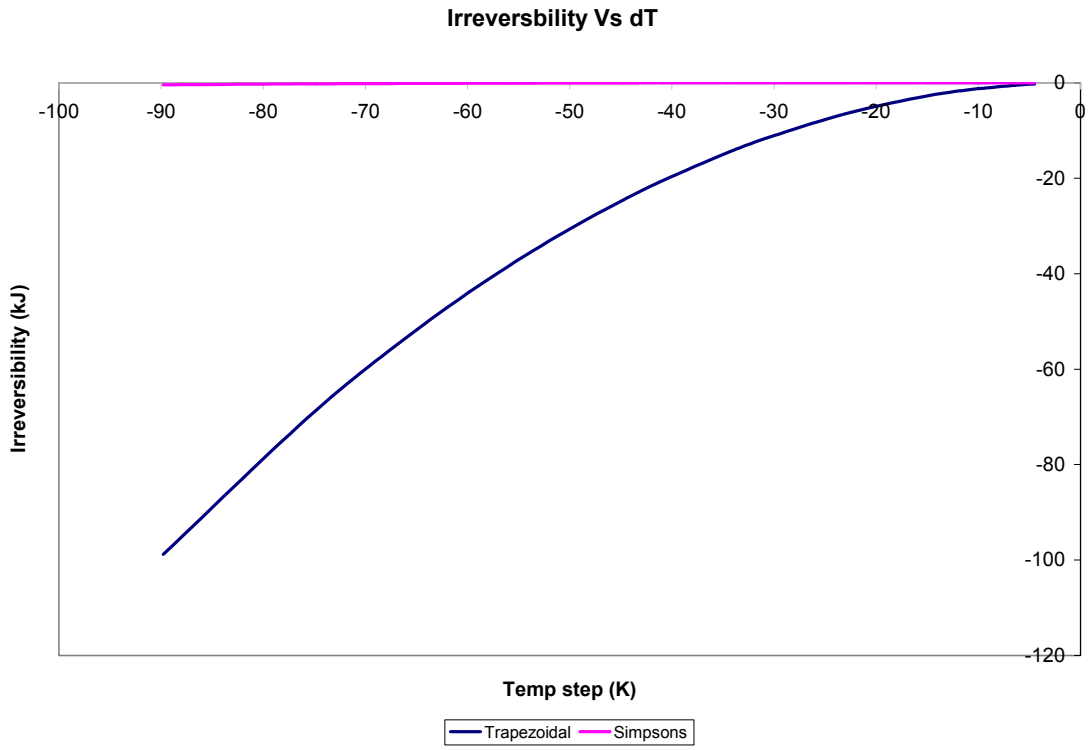

Fig. 13. Irreversibility of the ideal process as a function of temperature step size.

Fig. 14 is a plot of the total irreversibility of the system when $\int sdT$ is calculated from Simpson's rule. The irreversibility computed is a negligible fraction compared to the enthalpy of the reaction. A certain uncertainty is associated with the computation of the integral and $\int sdT$ and it is the cause for the low negative when the temperature step size is large. It can be seen that as the temperature step size decreases, meaning when more and more reactors are used the uncertainty reduces and the total irreversibility approaches zero. Irreversibility from Fig. 14 is seen to approach zero irreversibility for the theoretical limit of zero temperature step size.

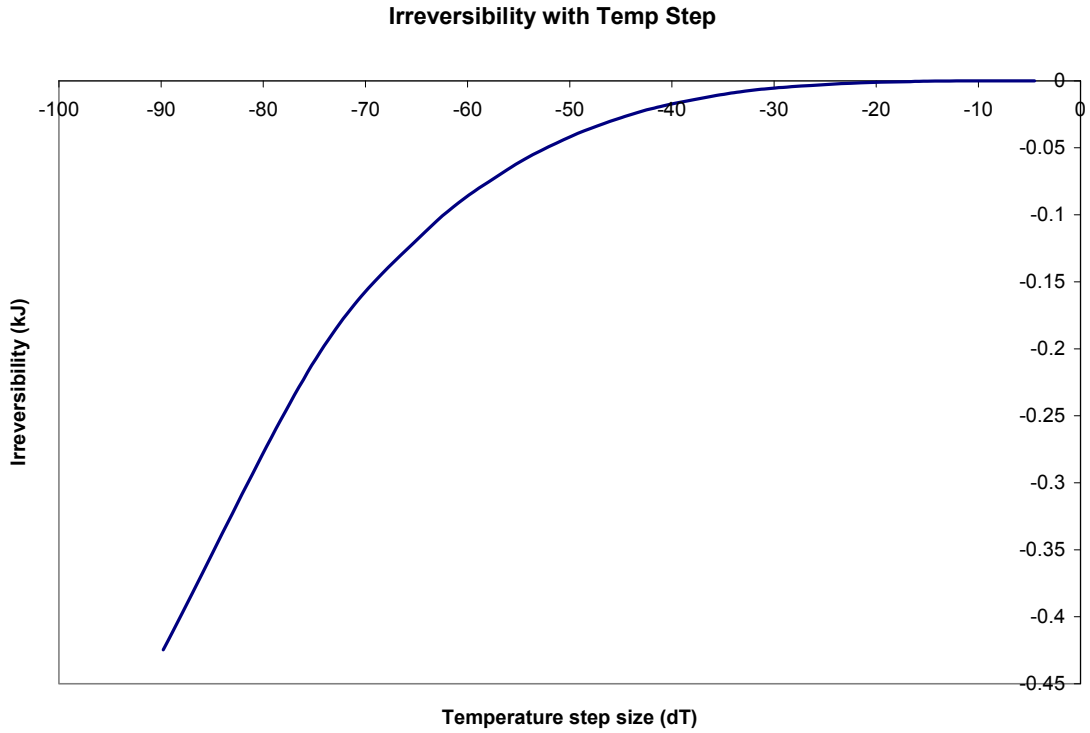

Fig. 14. Total irreversibility for the ideal process.

Net Work

In order to compare the process to a fuel cell, work extraction from the process is to be calculated. Availability balance gives the work output from the process. The availability balance requires the inlet composition, exit composition and thermodynamic properties are required. Table 2 shows the inlet composition for CV-2 along with the required properties. Table 3 shows the thermodynamic properties for species at 298°K that are used in availability analysis. Appendix IV shows the calculations for availability across CV-2 and CV-1. The work extracted from CV-2 is 672776 kJ and work input to CV-1 is calculated at 476099 kJ. Subtracting the work input to CV-1, we obtain the net work extracted from the whole scheme at 196677 kJ. The net work extracted for every kmole of H_2 burnt would be given as 223897 kJ

Table 2
Reactant species composition and properties at 5000°K

Species	Reactants (kmoles)	$\overline{h}_k(T)$ at 5000°K (kJ/kmole)	$\overline{s}_k^o(T)$ at 5000°K (kJ/kmole °K)
H_2	0.88	166759.2	222.54
O_2	0.44	180729.6	305.53
H_2O	0.12	550.1	315.96
N_2	1.88	167875.8	286.10

Table 3
Species properties at 298°K

Species	$\overline{h}_k(T)$ at 298°K (kJ/kmole)	$\overline{s}_k^o(T)$ at 298°K (kJ/kmole °K)
H_2	0	130.6
O_2	0	205.0
H_2O	-241820	188.7
N_2	0	191.5

If a fuel cell were running with the same input as the reactants supplied at 298°K and products as the mixture coming out of CV-2 at 298°K, availability analysis will give the same set of results as all the species composition and reactants would remain exactly the same.

Effect of Inert Gas on the Scheme

Futuregen is a new United States initiative to create the first zero-emissions fossil fuel power plant. It aims to integrate CO_2 sequestration and H_2 driven power production

using coal as the starting point. Coal gasification results in CO, a hydrocarbon, H_2, NH_3, N_2 and other products based on the chemical composition of the fuel gasified. Futuregen employs the reaction of these products with steam to form CO_2 and H_2 [12]. N is completely converted to N_2 and S atoms completely to SO_2. These pass through a bed where N_2 and Sulphur products are absorbed completely. The mixture leaving the bed would consist of CO_2 and H_2 at atmospheric pressure. Further CO_2 in Futuregen is sequestered leaving pure H_2. A simplified schematic of the Futuregen process is indicated in Fig. 15. Pure H_2 could be used in either a combined cycle plant or in a fuel cell for power production. It can be shown that N_{H_2}, the no of kmole of H_2 produced for every kmole of fuel having the chemical formula CH_hO_O is given by the empirical relation

$$N_{H_2} = 0.4115\ h - 0.6204\ o + 1.4776 \quad (47)$$

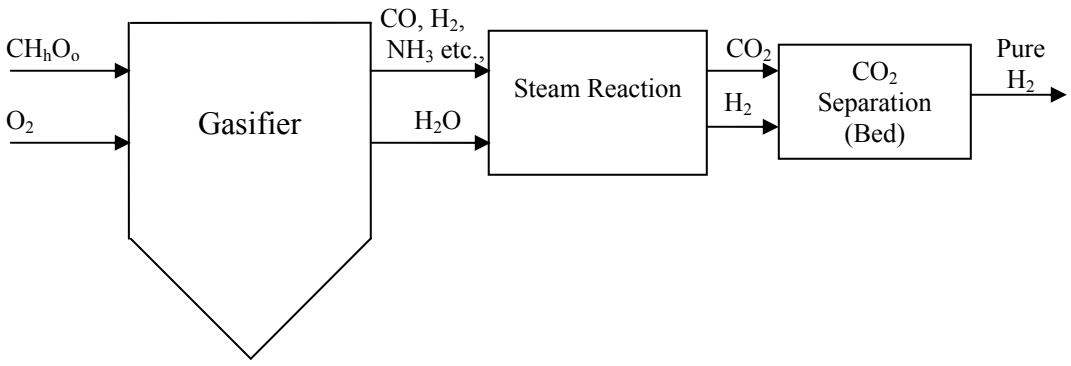

Fig. 15: Simplified schematic of Futuregen concept.

The following paragraph is a discussion on the affect of change in inert gas species on the change in the equilibrium composition and work extraction from the process.

On calculations it is noted that the equilibrium composition remains exactly the same. This is because the equilibrium constant equation considers only the total number of moles inert species and it does not matter as to the species itself. It can be observed from Appendix III that N_{N_2} can be replaced with N_{CO_2} and N_{O_2} remains the same, as long as

$N_{N2} = N_{CO2}$. Availability calculations show that the work extracted with N_{CO2} as the inert species is the same as with N_{N2} case. If availability difference for N_2 alone is calculated, the equation is $N_{N2}\psi_{N2,in} - N_{N2}\psi_{N2,exit} = N_{N2} * \left\{(\bar{h}_{298} - \bar{s}_{pk,1}) - (\bar{h}_{298} - \bar{s}_{pk,2})\right\}$. $\bar{h}_{298}$ is for the same species and gets cancelled. Expanding the entropies at partial pressures, RHS becomes $N_{N2} * (\bar{s}_{N2,2} - \bar{s}_{N2,1}) = N_{N2} * \left\{(\bar{s}_{298} - \bar{R}\ln(x_{N2,2}) - (\bar{s}_{298} - \bar{R}\ln(x_{N2,1})\right\}$ and finally

$$N_{N2}\psi_{N2,in} - N_{N2}\psi_{N2,exit} = N_{N2} * \bar{R}\ln\left(x_{N2,1}/x_{N2,2}\right) \quad (48)$$

$x_{N2,1}$ and $x_{N2,2}$ represent the mole fractions of N_2 at inlet and exit for the whole scheme. As the other species remain unchanged, mole fractions remain same. Thus the work extracted would be exactly the same irrespective of the inert species used as long as the molal composition does not change.

However, due to difference in thermodynamic properties of the different inert species, other mixture properties like *G* change. Fig. 16 plots the change in *G* of the mixture as a function of percentage of reaction progress. 0% would mean reactants just entering the first reactor in the system and 100% would mean the complete combustion of H_2 to H_2O. As can be seen, the CO_2 case is an approximate offset of the N_2 case. This is due to the enthalpy of formation being -393520 kJ/kmole for CO_2 and 0 kJ/kmole for N_2. Thus G of the mix is lower for CO_2 case when compared to N_2. Though irreversibility calculations are affected by a very small change, still the irreversibility reaches zero for small temperature intervals (as observed in Fig. 14) and work extracted for the scheme remains the exact same number.

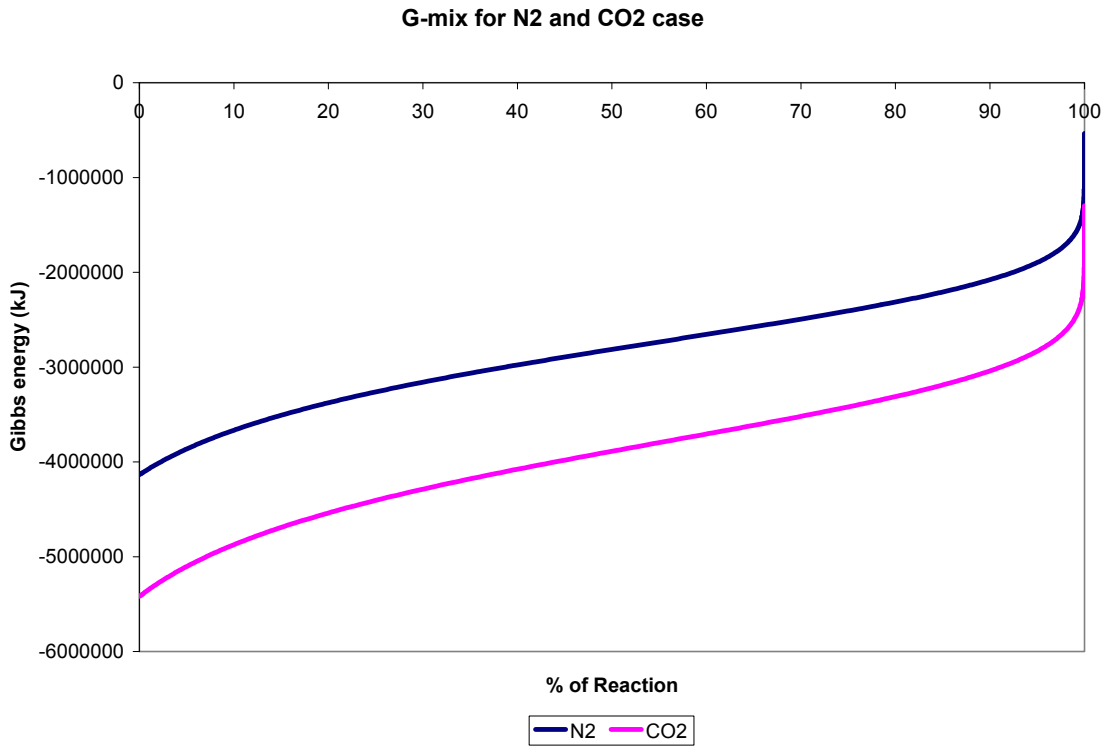

Fig. 16. Gibbs energy of reactant mixture for N_2 and CO_2 cases.

The fossil fuel used in Futuregen plants can vary according to fuel and location it is obtained from. The chemical composition determines the ratio of H_2 and CO_2 released from gasification after passing through the bed and is given by N_{H_2}. N_{H_2} is obtained from Eq (47) and includes H_2 obtained from fuel as well as from H_2O. As a reminder, the inert gas species does not change the work extraction from the scheme as long as the no of kmoles of the species remains the same. So, a comparison for the work output for different fuels (supplied to the gasifier) is required. The only change in using different

fuels would be the H_2: CO_2 ratio which can be calculated using equation eq (47). It must be remembered that before taking this ratio, the fuel must be written in the reduced form (CH_hO_O) which has only one atom of C. N_{H_2} gives the moles of H_2 liberated for every mole of CO_2 in the gasification product.

Fig. 17 is a plot of the H_2 and N_2 molal composition for the 5000°K reactor as a function of the mole fraction of the inert species. This composition is the reactant mixture as input to CV-1 in Fig. 9. The equilibrium composition at 5000°K is dependant on the input kmoles of the inert species. This changes the kmoles of H_2 as well as the mole fraction for each species. Fig. 17 shows the change in H_2 composition in the equilibrium mixture as a function of inert species mole fraction. For 1 kmole of H_2, stoichiometric air mixture yields 1.88 kmole of N_2. According to the equilibrium composition at 5000°K, N_2 mole fraction is 0.57. It can be seen that at low mole fraction of inert gas, change in N_2 kmoles has quite an effect on the change in H_2 composition in the mixture. As the mole fraction for inert gas keeps increasing, the effect of N_2 on H_2 keeps reducing till about it reaches the stoichiometric fraction for N_2. The effect of N_2 beyond this quite small as there is little change in H_2 kmoles in the composition even with a high change in kmoles of N_2. This trend can be seen in Fig. 17 also shows N_2 composition along with H_2 as a function of the mole fraction of the inert gas. Remember that this trend is applicable to any inert gas that replaces N_2.

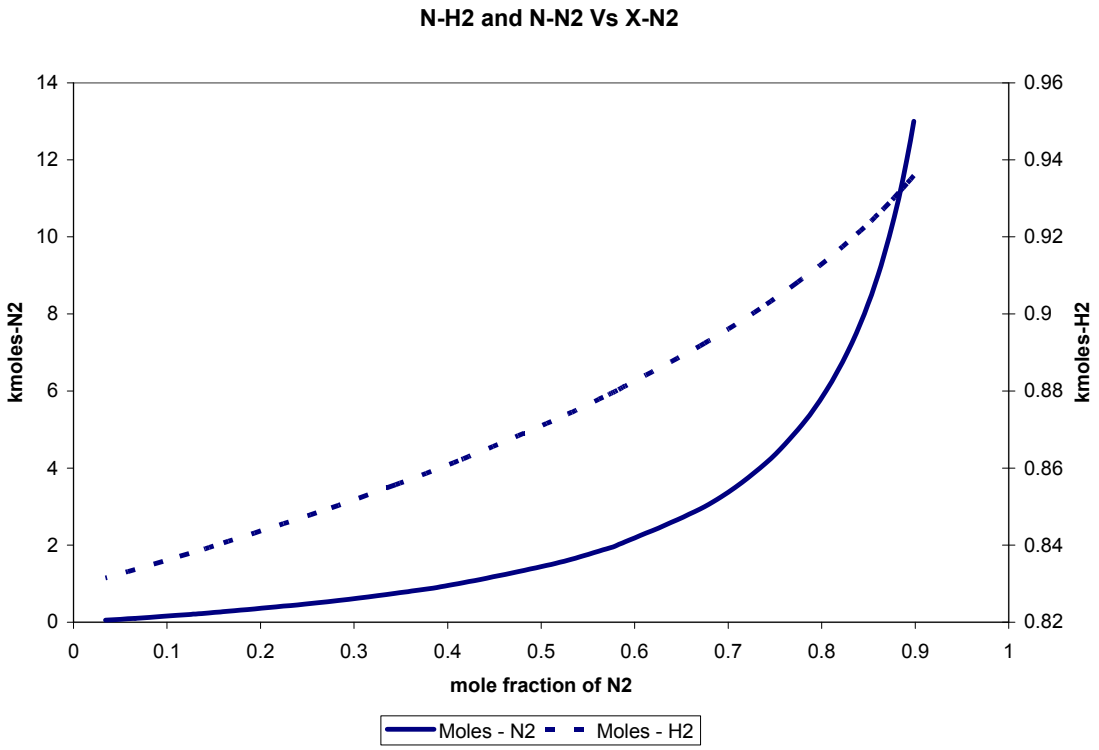

Fig. 17. Effect of inert gas composition on the equilibrium mixture.

Fig. 18 is a plot of W_{opt}, or work extraction from the ideal process against the mole fractions of N_2. As the initial composition changes for different dilutions, the work extracted is normalized per kmole of H_2 fuel burnt. It can be observed from the figure that the work extracted reduces as the inert gas dilution increases. Eq. (48) gives the change in availability of inert gas keeping the other species same. As $x_{N_2,1}$ increases, the ratio $\left(x_{N_2,1}/x_{N_2,2}\right)$ reduces in Eq. (48) and contributes to the decrease in work of the system. Fig. 18 also shows the overall efficiency (per kmole of H_2 combusted) of the system for inert gas dilution. As with work extraction and system efficiency reduces with increase in the mole fraction of the inert gas.

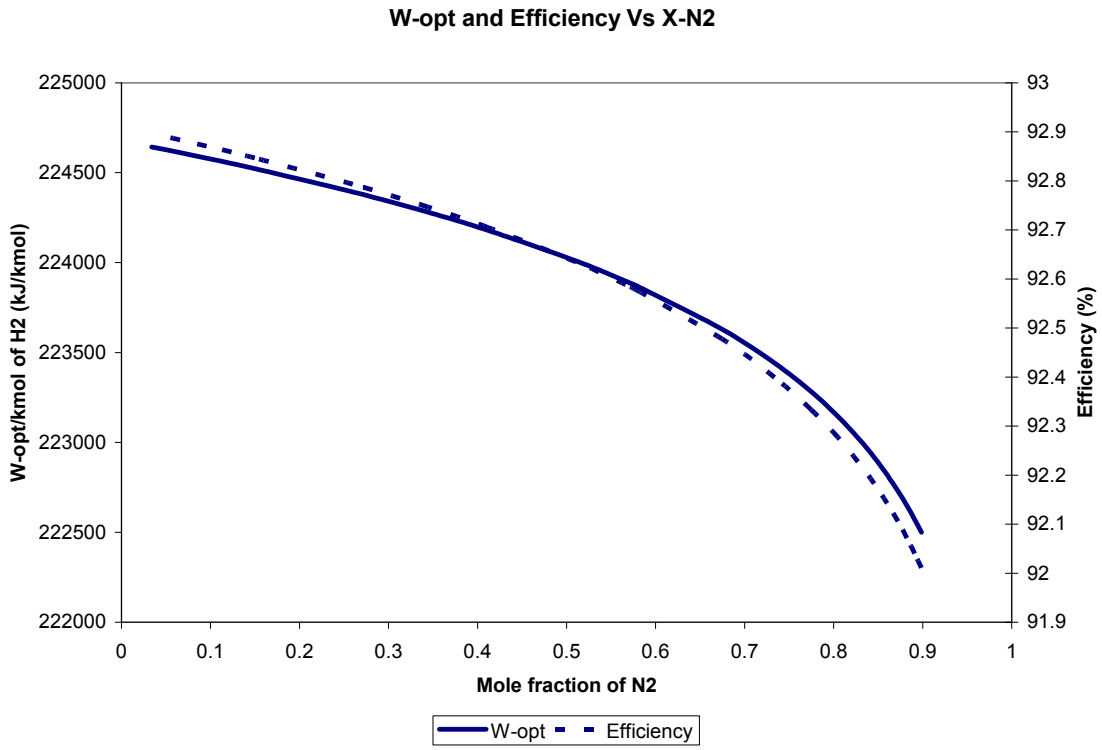

Fig. 18. Work output and efficiency of the proposed process with change in inert gas composition.

Effect of Pressure on the Scheme

Fig. 19 is a plot for the work extraction from system for different pressures. It was seen that the starting composition with 5000°K reactor is different for different pressures. In order to compare the work extraction in different cases, they must be computed for every kmole of H_2 that enters the reactor. A little caution has to be exercised in reading Fig. 19. It shows W_{opt} normalized with input fuel for various pressures. It can be seen that as the pressure of the system increases, the overall work extracted from the system increases. There is a little effect of pressure variation as work extraction change is less than 2% when system pressure is changed from 0.5 bar to 100 bar. Within this small change, most of the variation takes place within p=3 bar. Fig. 19 also has a plot for change in the overall efficiency of model (per kmole of H_2 entering the system) for

different pressures. The efficiency of the process tracks very close to the work extraction from the system. Notice that efficiency changes from 92.4% at p=0.5 bar to 93.6% at p=100bar. This variation is significantly small compared to the huge change in pressure the system is being subjected to. As with W_{opt}, change in efficiency is marked below a system pressure of 3 bar.

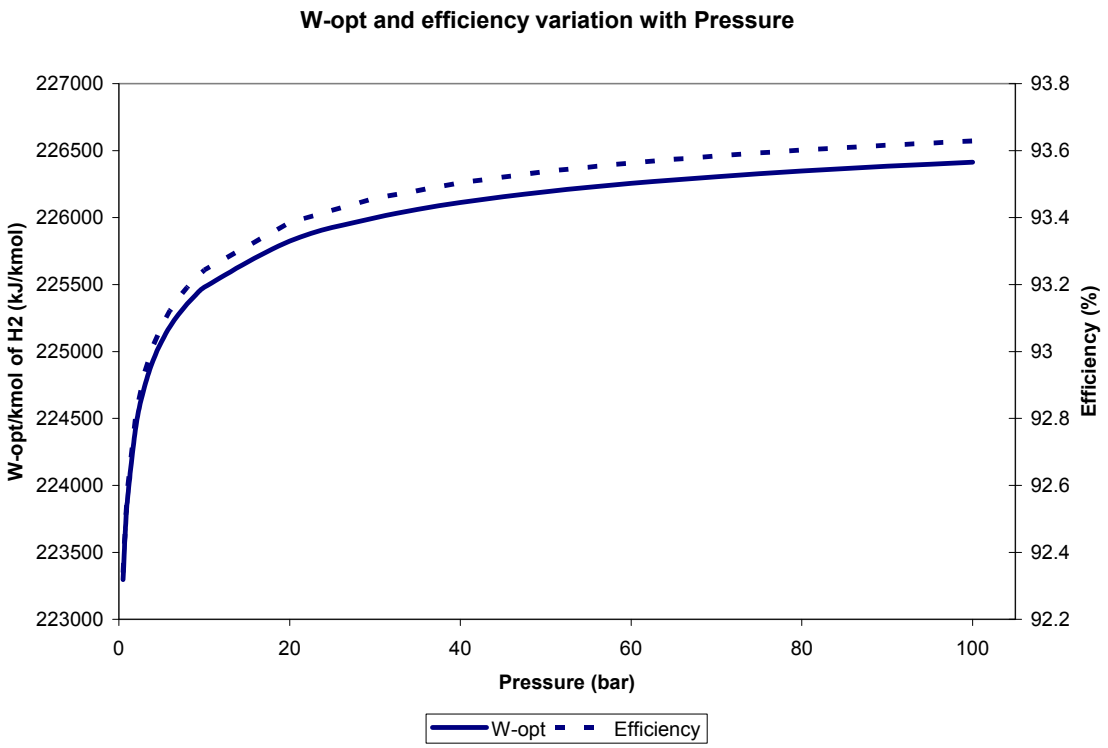

Fig. 19. Work output and efficiency of the proposed scheme for various system pressures.

Other Considerations

The reactants for the process are assumed to be supplied at their partial pressures. There is a certain irreversibility associated with obtaining the reactant mixture for the process which has been ignored in the discussion. As there is a comparison between a fuel cell and the ideal process, both have the same starting reactant mixture and the effort in obtaining that mixture is the same in both cases. In the case of the ideal process, a certain starting energy is to be supplied in order to heat the reactants from 298°K to 5000°K and from then on the process can run as a perpetual machine.

If the idealized process were to be applied for practical energy conversion, a lot of factors need to be considered. Primary is that of the heat exchangers needed for energy transfer from chemical reactor to the heat engine. Pumping and other heat losses will occur and an overall decrease in efficiency of the process occurs. For the practical operation of a fuel cell, numerous auxiliaries are required. Thermal and water management are required for efficient running of the fuel cell. These combined with other ohmic losses and voltage drops decrease its efficiency.

Scheme Applied to Other Fuels

An attempt was made to apply the hypothetical scheme to other common fuels like Acetylene (C_2H_2) and Methane (CH_4). The hypothetical model does not quite fit such fuels because almost all the reactant converts to products at the starting temperature of 5000°K itself. In cases for C_2H_2 and CH_4 almost 98% of the fuel gets converted to products at 5000°K. Thus other temperature steps will hardly have any reactant left and would be of no thermodynamic interest. However, such a model could be appropriate for a higher temperature scheme, but specific heat tabulated above is not valid for temperature for 5000°K. Thus it is hard to determine at what temperatures significant amount of reactant is still left.

SUMMARY AND CONCLUSIONS

Summary

A theoretical process was formulated for minimizing the irreversibility caused due to chemical reaction and heat transfer. A hypothetical model was constructed to compute the net work that can be extracted from the ideal process. Thus, the efficiency of the ideal process was compared to that of a fuel cell for the same chemical reaction. When carried over a large number of steps, the ideal process can extract as much work as a fuel cell can, both having the same reactants.

Products of the Futuregen process have a mixture of H_2 and CO_2 whose composition is based on the fuel (coal) used for gasification. CO_2 acts as the inert gas. A parametric study was conducted on the above ideal process for different ratios of H_2: CO_2 mixture. The study determines that there is no effect of species change of the inert gas on the equilibrium composition. The efficiency of the process does not improve much with decrease in inert gas composition. Also, there is not a marked improvement in efficiency with increase in the pressure of the process.

Conclusions

- In the theoretical limit, there exits an ideal process that can extract work from thermal energy released by chemical reaction which is as efficient as an ideal fuel cell when both the processes have the same chemical reaction.
- The removal of inert gas does not significantly increase the efficiency for the ideal process.
- The system pressure does not have a marked effect on the efficiency of the ideal process.

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APPENDIX I

Ideal work extraction from exhaust gases liberated from adiabatic combustion.

Input to the adiabatic combustor is 1kmole of H_2, 0.5 kmole of O_2 and 1.88 kmole N_2 at 298°K. The overall chemical reaction for combustor is $H_2 + 1/2O_2 + 1.88N_2 \rightarrow H_2O + 1.88N_2$. Just before reactants enter the reactor, mole fraction X_{H_2}=1/ (1+0.5+1.88) = 0.296. Similarly X_{O_2}=0.148 and X_{N_2}=0.556. Ψ for each species is calculated using the equation $\psi_k = \bar{h} - T(\bar{s} - \bar{R}\ln(x_k))$. For the whole mixture $\psi_1 = N_{H_2}\psi_{H_2} + N_{O_2}\psi_{O_2} + N_{N_2}\psi_{N_2}$. This is calculated as -184,920 kJ.

Adiabatic flame temperature is obtained by considering the energy balance. $dE_{c.v}/dt = \dot{Q}_{c.v} - \dot{W}_{c.v} + \sum_{in} \dot{N}_k\bar{h}_k - \sum_{exit} \dot{N}_k\bar{h}_k$ with the assumption of negligible potential and kinetic energies in the first law open system rate equation. Adiabatic conditions and no work extraction cancel the first two terms on the RHS. Steady state reduces LHS to zero. So it reduces to $\sum_{in} N_k\bar{h}_k = \sum_{exit} N_k\bar{h}_k$ on mole basis. This equation needs to be solved iteratively to find the temperature for products being 1 kmole of H_2O and 1.88 kmole of N_2.

Solution gives T_{ad}=2,528.7°K. At this temperature the availability of products can be found out using $\psi_2 = N_{H_2O}\psi_{H_2O} + N_{N_2}\psi_{N_2}$ with the mole fraction X_{H_2O}=0.347 and X_{N_2}=0.653. ψ_2 is calculated as -233,079 kJ per kmole of H_2 reacted.

The optimum work that could be extracted in the adiabatic combustor is given by $\bar{W}_{opt,1-2} = \psi_1 - \psi_2$. $\bar{W}_{opt,1-2}$=48159 kJ. But there is no work extraction in the adiabatic combustor and hence is called lost work. As irreversibility is defined as $I_0 = T_0 * \sigma_{c.v}$, entropy generation for the combustor is $\sigma_{c.v} = I_0 / T_0$ =48,159/268 =162 kJ/ °K per kmole of H_2 that is combusted.

From the gaseous products of adiabatic combustion at T_{ad}, work is extracted through a series of heat engines running at close temperatures to remove irreversibility. The final state of gases is 1kmole of H_2O and 1.88 kmole of N_2 at 298°K. The mole fractions remain X_{H2O}=0.347 and X_{N2}=0.653 as there is no change in chemical composition and ψ_3 is calculated as -408,259 kJ per kmole of H_2 burnt.

The optimum work that is extracted from the series of heat engines is given by $\bar{W}_{opt,2-3} = \psi_2 - \psi_3$. $\bar{W}_{opt,2-3}$ = 175,180 kJ per kmole of H_2 reacted in the combustor.

Total heat supplied to the engines is difference in enthalpy of products from adiabatic temperature to ambience (from adiabatic combustion H_1=H_2). H_1 is calculated using $H_1 = N_{H2}\bar{h}_{H2} + N_{O2}\bar{h}_{O2} + N_{H2O}\bar{h}_{H2O}$. All enthalpies are at 298°K. H_1 is computed to be 0 as all species are in natural form and enthalpy of formation is zero for each. H_3 which is the enthalpy of species at 298°K following work extraction is given by $H_3 = N_{H2O}\bar{h}_{H2O} + N_{N2}\bar{h}_{N2}$ and is calculated as H_3 = -241,820. Heat supplied to reactors is given by Q=H_1-H_3. Q is 241,280 kJ per kmole of H_2 supplied to the reactor.

The overall efficiency is given by $\bar{W}_{opt,2-3}$/Q =175180/241280 = 72.4%.

Maximum available work between states 1 and 3 is given by $\bar{W}_{opt,1-3} = \psi_1 - \psi_3$. $\bar{W}_{opt,1-3}$=-184920-(-408259) = 223,339 kJ per kmole of H_2 burnt.

Availability efficiency is defined as $\bar{W}_{opt,2-3} / \bar{W}_{opt,1-3}$ = 78%.

APPENDIX II

Derivation of equivalent Carnot temperature ($T_{C,B}$)**.**

The maximum work that can be extracted from hot product gases from adiabatic combustion (for every kmole of H_2 combusted) is given by

$$\bar{W}_{opt} = \sum_{\mathrm{Pr}od} N_K \bar{\psi}_k(T_{ad}, p_k) - \sum_{\mathrm{Pr}od} N_K \bar{\psi}_k(T_o, p_k)$$

$$\bar{W}_{opt} = \sum_{\mathrm{Pr}od} N_K(\bar{h} - T_{ad}\bar{s}_k(T_{ad}, p_k)) - \sum_{\mathrm{Pr}od} N_K(\bar{h} - T_o\bar{s}_k(T_o, p_k))$$

$$\bar{W}_{opt} = H_P(T_{ad}) - H_p(T_o) - T_o(S_p(T_{ad}, p_k) - S_p(T_o, p_k))$$

Due to adiabatic combustion H_R (T_o) = H_P (T_{ad}). Adding and subtracting S_R (T_o,p_k)

$$\bar{W}_{opt} = H_R(T_o) - H_p(T_o) - T_o(S_p(T_{ad}, p_k) - S_R(T_o, p_k) + S_R(T_o, p_k) - S_p(T_o, p_k))$$

$$\bar{W}_{opt} = -\Delta H_R(T_o) - (T_o(S_p(T_{ad}, p_k) - S_R(T_o, p_k)) + T_o\Delta S_R(T_o, p_k)$$

Observe that the term $(S_p(T_{ad}, p_k) - S_R(T_o, p_k))$ is the change in entropy or entropy generation σ_{ad}. Equation is re-written as

$$\bar{W}_{opt} = -\Delta H_R(T_o) - T_o\sigma_{ad} + T_o\Delta S_R(T_o, p_k)$$

The overall heat available for conversion is from H_P (T_{ad}) or H_R (T_o) to H_P (T_o) which is (ΔH_R (T_o)). If a single heat engine were to be used for converting this energy to work, Work extraction is

$$\bar{W}_{opt} = -\Delta H_R(T_o)\left(1 - \frac{T_o}{T_{C,B}}\right)$$

Equating both works to find $T_{C,B}$

$$\Delta H_R(T_o)\left(\frac{T_o}{T_{C,B}}\right) = -T_o\sigma_{ad} + T_o\Delta S_R(T_o, p_k)$$

Finally,

$$T_{C,B} = \frac{-\Delta H_R\big|_{T_o}}{-\Delta S_R\big|_{T_o} + \sigma_{ad}}$$

For the reaction H_2+½O_2+1.88N_2→H_2O+1.88N_2,

$-\Delta H_R\big|_{T_o}$ = 241820 kJ.

$-\Delta S_R\big|_{T_o}$ = 56.14 kJ/ °K

From Appendix I, the entropy generation σ_{ad} = 162 kJ/°K

Using these values in the above equation to solve for $T_{C,B}$

$T_{C,B}$ = 1108.5 °K

APPENDIX III

The following is the detailed derivation for equation used in solving the equilibrium composition for fixed input atoms and given temperature.

Let N_H, N_O and N_N be the kmole of Hydrogen, Oxygen and Nitrogen atoms supplied to an isothermal reactor maintained at temperature T and pressure P. Let y, z and w be the no of kmole of O_2, H_2O and H_2 respectively in the product mixture. N_{N_2}, the kmole of N_2 in products is fixed because it is the inert species. The overall reaction is $N_N, N_O, N_H \rightarrow yO_2 + zH_2O + wH_2 + N_{N_2}N_2$. Mass balance on O and H gives

$$N_H = 2z + 2w \Rightarrow w = \left(N_H/2\right) - z$$

$$N_O = 2y + z \Rightarrow y = (N_O - z)/2$$

The equilibrium reaction considered for the system is $H_2O \Leftrightarrow H_2 + 0.5O_2$. The equilibrium constant relation is used as the third equation in the solution given by

$$K^o(T) = \frac{P_{O_2}^{1/2} P_{H_2}}{P_{H_2O}} = \exp\left(\frac{-\Delta G_T^o}{\bar{R}T}\right)$$

For a total pressure of P, if all species are considered ideal, the total no of moles in the products is $N = y + z + w = N_H/2 + N_O/2 + y$

Expanding the partial pressure for the species and writing all species in terms of y,

$$K^o(T) = \frac{y^{1/2}\left(N_H/2 - N_O + 2y\right)}{\left(N_O - 2y\right)}\left(\frac{P}{P^O N}\right)^{1/2} = \frac{y^{1/2}\left(N_H/2 - N_O + 2y\right)}{\left(N_O - 2y\right)}\left(\frac{P}{P^O\left(\frac{N_H + N_O}{2} + y\right)}\right)^{1/2}$$

$$\left\{\left(No - 2y\right)K^o(T)\right\}^2\left\{\frac{N_H + N_O}{2} + y\right\} = y\left(N_H/2 - N_O + 2y\right)^2\left(\frac{P}{P^o}\right)^{1/2}$$

$$\left\{K^o(T)\right\}^2\left\{No^2 + 4y^2 - 4Noy\right\}\left\{\frac{N_H + N_O}{2} + y\right\} = y\left(N_H/2 - N_O + 2y\right)^2\left(\frac{P}{P^o}\right)$$

Let $A=N_H/2+N_N/2$ and $B=N_H/2-N_O$

$$\left\{K^o(T)\right\}^2 \left\{No^2 + 4y^2 - 4Noy\right\}\left\{A + y\right\} = y\left(B + 2y\right)^2\left(\frac{P}{P^o}\right)$$

$$\left\{K^o(T)\right\}^2 \left\{ANo^2 + 4Ay^2 - 4ANoy + No^2 y + 4y^3 - 4Noy^2\right\} = \left(B^2 y + 4y^3 + 4By^2\right)\left(\frac{P}{P^o}\right)$$

Equation is re-written as $a_3 y^3 + a_2 y^2 + a_1 y + a_0 = 0$. The coefficients given as

$$a_3 = \left(4\frac{P}{P^o} - 4\left(K^o(T)\right)^2\right),\ a_2 = \left(4B\frac{P}{P^o} - 4A\left(K^o(T)\right)^2 + 4\left(K^o(T)\right)^2 No\right)$$

$$a_1 = \left(B^2\frac{P}{P^o} + 4\left(K^o(T)\right)^2 ANo - No^2\left(K^o(T)\right)^2\right),\ a_0 = -ANo^2\left(K^o(T)\right)^2$$

where $A=N_H/2+N_N/2$ and $B=N_H/2-N_O$.

Notice that a_3 tends to zero at P=1bar and K^o (T) =1. The equation at this point reduces to a quadratic equation. Use of the above equation for solution yields erroneous results. So results for quadratic case are used in case of the above situation.

Maximum NO_2 =input NO_2 +input $N_{H_2O}/2$.

Negative results for 'y' are ignored. If one of the roots for y exceeds maximum NO_2, it is ignored and the next root is selected.

APPENDIX IV

Availability calculations for the model.

Reactant composition entering CV-1 at 298°K: N_{H_2}=0.88 kmole, N_{O_2}=0.44 kmole, N_{H_2O}=0.12 kmole and N_{N_2}=1.88 kmole. Mole fraction of H_2, X_{H_2}=0.88/(0.88+0.44+0.12+1.88)=0.26. Similarly X_{O_2}=0.13, X_{H_2O}=0.04 and X_{N_2}=0.57. Availability of H_2 for this composition is $\psi_{H_2} = \bar{h}_{H_2} - 298(\bar{s}_{H_2} - \bar{R}\ln(X_{H_2}))$. ψ_{H_2} is calculated to be -42,203.42 kJ/kmole of H_2.

Enthalpy values for required species at 5000°K and 298°K are provided in Table 2 and Table 3 respectively

Availability at entrance to CV-1 is given by $\psi_1 = \psi_{H_2}N_{H_2} + \psi_{O_2}N_{O_2} + \psi_{H_2O}N_{H_2O} + \psi_{N_2}N_{N_2}$. ψ_1 = -213,274.54 kJ.

Availability for H_2 at the exit of CV-2 is calculated by using $\psi_{H_2} = \bar{h}_{H_2} - 5000(\bar{s}_{H_2} - \bar{R}\ln(X_{H_2}))$. ψ_{H_2} at exit to CV-1 is 97,148.73 kJ/kmole of H_2.

Availability at exit of CV-1 calculated using $\psi_2 = \psi_{H_2}N_{H_2} + \psi_{O_2}N_{O_2} + \psi_{H_2O}N_{H_2O} + \psi_{N_2}N_{N_2}$ = 262,824.08 kJ.

ψ_2 is also the availability at for entrance of CV-2.

At exit of CV-2 the products are N_{H_2O}=1 kmole and N_{N_2}=1.88 kmole at 298°K. Mole fraction of H_2O, X_{H_2O}=1/(1+1.88) = 0.35 and X_{N_2} = 0.65. . Availability of H_2 for this composition is $\psi_{H_2O} = \bar{h}_{H_2O} - 298(\bar{s}_{H_2O} - \bar{R}\ln(X_{H_2O}))$. ψ_{H_2O} at exit of CV-2 is -300,679.31 kJ/kmole of H_2O.

Total availability at exit to CV-2 is calculated as $\psi_3 = \psi_{H_2O}N_{H_2O} + \psi_{N_2}N_{N_2}$ =-409,951.92 kJ.

Work extracted from CV-2 is given by $W_{c.v\text{-}1} = \psi_2 - \psi_3 = 262{,}824.08\text{-}(\text{-}409{,}951.92) = 672{,}776$ kJ.

Work supplied to CV-1 for raising the temperature of reactants from 298°K to 5000°K is given by $W_{c.v\text{-}2} = \psi_1 - \psi_2 = \text{-}213{,}274.54\text{-}262{,}824.08 = \text{-}476{,}098.62$ kJ. Negative value indicates work supplied

Net work extracted from the model $W_{net} = W_{c.v\text{-}1} + W_{c.v\text{-}2} = 196{,}677.38$ kJ.

Net heat supplied for work extraction is
$Q = H_R\,(298) - H_P\,(298) = \text{-}\,29{,}398.68\text{-}(\text{-}241820) = 212{,}421.32$ kJ

Net efficiency of the system is $W_{net}/Q = 92.59$ %.

VITA

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